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ORIGINAL PAPERS

VARIATIONS IN GLASS CAUSED BY HEAT TREATMENT[1]

By A. Q. Tool and C. G. Eichlin

ABSTRACT

The exothermic and endothermic effects detectable from the forms of the heating curves of a glass vary in magnitude depending on the previous heat treatment. With many of the common glasses, these variations bear a relatively simple relation to any changes in this treatment, but with others the relationship is not so easily established. Some glasses which are exceptional in this respect have a rather high silica content. It is shown in this paper that the previous heat treatment is always the chief determining factor in these variations. It should be possible therefore to obtain considerable information relative to the treatment a glass sample has received by simply studying such curves. It should also be possible to study in the same way, the relative effectiveness of the various heat treatments which may appear desirable.

It is further shown that the density is affected by the heat treatment and in the discussion reasons are given for believing that many of the other properties of glass may be varied by the same means. In this connection some speculative views as to the nature of glass are included as aids toward explaining effects already observed and also for suggesting others which should be sought.

Introduction

It has been shown[2] that the heat treatment a glass has received affects the form of its heating curve on reheating. This occurs in that region of abnormal heat absorption commonly found near those temperatures usually chosen for annealing. The variations in the heating curves resulting from the different heat treatments given the glass in its manufacture are so marked that it is often possible, from a study of these curves, to determine the effectiveness of the annealing treatment. With most glasses in common use the forms of their heating curves and the changes caused by altering their heat treatments are relatively simple and easily analyzed. It is possible in such cases to show that the variations so caused are also consistent and reproducible.

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[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce. Recd. Oct. 25, 1924.

[2] *Jour. Op. Soc. Amer.*, **4**, 340 (1920); *Jour. Op. Soc. Amer. & Rev. Sci. Inst.*, **8**, 419 (1924).

Typical Heating Curves

This type of heating curve is depicted in Fig. 4. Curve 13, obtained on an original specimen of sheet glass, shows the type usually found on testing a reasonably well-annealed commercial product. Curve 14 results when the same glass is annealed much more carefully, while curve 15 is typical when the glass has been cooled very rapidly. The method employed in obtaining these curves and the possible significance of the exothermic effect at temperatures just below that corresponding to the point *A* for the chilled glass and of the endothermic effect between the *A* and *B* temperatures for all three samples have been fully described and discussed in the articles noted, and consequently will not be considered in all their details in the present paper.

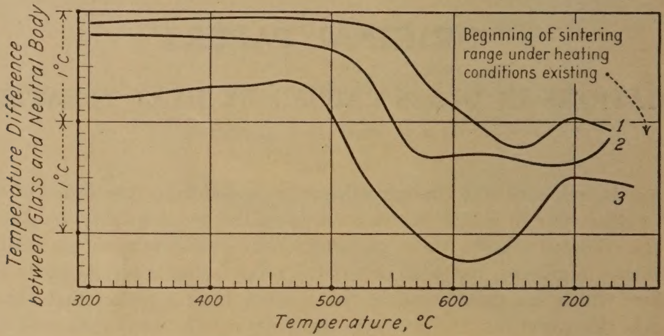

FIG. 1.

Consistency and Reproducibility of the Curves

It has been found in most cases[1] with glasses ranging from those used in common containers to those used for optical purposes, that neither the position nor breadth of range of the endothermic effect in a given glass varies materially under standard testing conditions (never more than a few degrees) with the character of the previous heat treatment. The differences in the form and appearance of the heating curves may be even more extreme than shown in Fig. 4 due mostly to the changes in magnitude of the thermic effects produced through controlling the previous heat treatment of the glasses. The gradations to be obtained between the most extreme forms are also practically innumerable. In spite of this it is still easy to reproduce practically any one of these curves on any other sample of the same glass by properly re-treating it. This is usually the case even after the sample has been carried through a long cycle of chillings and annealings.

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[1] Some apparent exceptions have been noted, of which those of light flint, light and heavy barium crown have been mentioned previously (*loc. cit.*). In the case of the barium crowns the variations were probably due to deterioration.

There are some glasses, however, from which it is apparently much more difficult to obtain data showing this consistency. Such difficulties are to be expected with certain opals, many enamels and glazes and similar near glasses, since they are usually incompletely vitrified or of types that devitrify easily. Certain of the well-known real glasses also offer such difficulties, since they differ noticeably from the majority in regard to the definiteness of form of the heating curve and the simplicity of the changes caused by altering the heat treatment. Some of the glasses having a high silica content, *e. g.*, those similar to pyrex, fall in this class. With some of the glasses which show this lack of consistency, certain treatments cause a marked shift of the range of the endothermic effect. This often is accompanied, though not always, by a tendency of the glass to devitrify.[1] With others, notably some of those high in silica, the range of

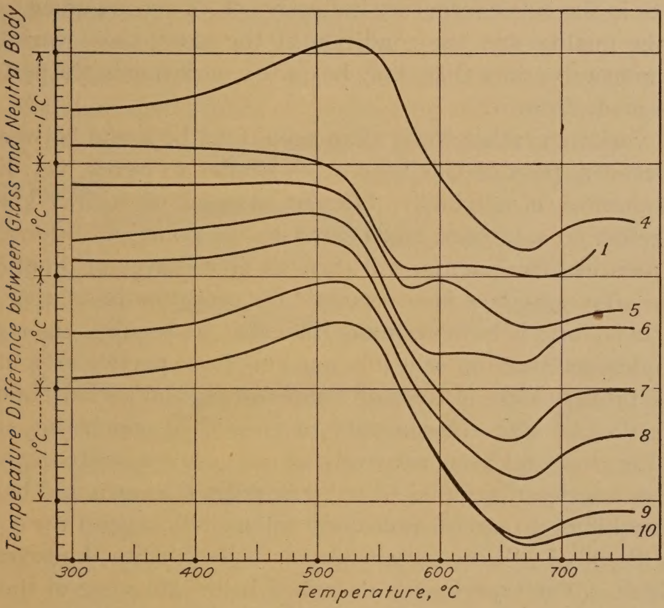

FIG. 2.

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[1] If devitrification actually occurs, it has been found from all previous experience practically impossible to restore the endothermic effect to the original temperature range by any heat treatment short of remelting.

the endothermic effect not only tends to shift but also to increase to abnormal widths, appearing occasionally to divide into two distinct ranges. These variations, sometimes accompanied by apparently complicated exothermic effects, often result in curves which are difficult to reproduce.

The curves shown in Figs. 1 and 2 obtained with pyrex and a somewhat similar glass of foreign make are samples of the variety of forms which such glasses yield. Although the majority of these curves were obtained with treated samples, all of them have been practically duplicated on originals. These figures show the great multiplicity of curve forms obtainable, and further tests will undoubtedly increase their number. If the changes in the curve forms are indicative of, or accompanied by, differences in the quality and the condition of the glass, these variations become of importance, since there may be quite a variation in the performance of articles made from it.

While a variation rather wider than usual may be found between different samples of a glass of this type, *i. e.*, similar to pyrex, yet, like most glasses, a number of originally different samples of such a glass when placed together in a furnace and heated to the point of sintering before receiving identical treatments, will then all give curves of practically the same form. To reproduce in any sample the condition in another yielding a certain curve form is however more difficult. It requires the equivalent of some unknown treating schedule and involves, particularly in certain ranges, the proper choice of treating temperatures and periods, and cooling rates. To do this with the majority of glasses, of which the one represented in Fig. 4 is typical, is relatively simple, since a study of the curves obtained on a series of samples whose treatment is known and has ranged from severe chilling to careful annealing[1] will usually suggest the equivalent treatment required. With certain glasses high in silica, however, this is more difficult. The experiments described below are some of those made to show that all the curve forms found on different original specimens of such a glass can be reproduced on any one of the specimens by properly treating it. They were made to determine also whether or not there was a definite permanent difference in the various specimens due to variations in the composition or to other factors, such as deterioration during use or heat treatment, etc. It appears, from experience gained during these tests, that the variations in the curve forms are for the most part due only to removable differences in the condition of the glass caused by the heat treatment received and that after sufficient data have been collected a heat treatment can be chosen which should bring the glass practically to any condition normally possible. These conditions are innumerable, each being determined by the "effective" annealing temperature, at which temperature the glass is probably in a state of practical equilibrium.

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[1] Such a series of samples would give curves somewhat similar in appearance to those shown in Fig. 2, of the article "Certain Effects Produced by Chilling Glass," *Jour. Op. Soc. Amer. & Rev. Sci. Inst.*, **8,** 428 (1924).

Experimental Methods and Results

Since the methods used in obtaining the heating curves shown here have been described fully in the references cited, it will suffice to say that they differ but little from the differential thermocouple method ordinarily used in the detection of exothermic and endothermic effects in other materials. In order to compare a number of curves obtained in this way on various specimens or samples it is always advisable to use the same heating rate and methods of packing the samples in the furnace, and also to maintain all other conditions as nearly the same as possible. This usually requires that the tests be made in sequence and that the samples be changed with a minimum disturbance of the packing and containers and obviously also with no appreciable alterations in the apparatus used.

Preparation of Sample In preparing the glass for these studies a large quantity of each specimen was broken into bits and after discarding the finer particles and larger pieces those retained averaged about 1 mm. in diameter. This prepared glass was thoroughly mixed and divided into a number of samples for the various treatments proposed.

Heating Rates The heating rates in the following tests were in all cases approximately 6.5°C per minute. The observations on the actual temperatures of the glass were taken at ten-minute intervals, intermediate temperatures being obtained by interpolation; while those necessary to determine the temperature differences between the glass and neutral body were taken at approximately 12°, 6°, or 3° intervals, depending on the rapidity with which this difference changed. Usually the heating was continued until those temperatures were reached where incipient sintering caused variations in this temperature difference. With samples of a uniform character and under standard heating and packing conditions this point is fairly definite but changing these factors alters it somewhat.

Plotting of Curves In the curves as plotted the variations in the ordinates represent the changes in the difference in temperature between the glass and neutral body, while the abscissae indicate the actual temperatures of the glass. The lines showing the trend of the curves include within their width all the points representing the observations. To prevent entanglement and to make comparison easy the curves have been shifted arbitrarily one above the other. This is permissible since it is the variation of the ordinate and not its absolute value which is of importance.

Curves for Pyrex Glass

In Fig. 1, curve 1 was obtained on the original (*i. e.*, untreated) glass from a pyrex beaker. This curve shows practically no trace of what sometimes appears to be a second heat absorption region (590° to 680°C); the first one, however, (520° to 570°C) is quite definite. In fact, no curve was obtained on pyrex in which evidence of this first absorption region was missing. Curve 2 was obtained under similar conditions on an untreated sample from a flask made from a foreign glass, high in silica and somewhat similar to pyrex in its characteristics. The two curves appear quite dissimilar; however, the latter does not differ to the same degree from other curves that have been obtained on other samples of pyrex. One of the chief differences to be observed between the two curves is that the first indication of an absorption region occurs about 20° higher in 2 than in 1. This eliminates in part the first absorption region in the former, and probably enhances the indication of a second region.

Curve 3 was obtained on this same foreign glass, after it had been heated for one hour at 700°, cooled in $^1/_2$ hour to 520°, annealed about twenty hours in the range 520° to 510°, cooled to 490°C in seven hours, and then rapidly to room temperature. This curve indicates that by this treatment the magnitude of the heat absorption has been greatly increased and that the temperature at which it begins has been reduced about 50° (to 490°C); or almost 30° lower than the temperature at which it usually begins in pyrex. It has also been found that the same treatment of pyrex produces a curve of similar form, together with a reduction of the beginning temperature of the absorption.

In Fig. 2, curve 4 was obtained on part of the specimen giving curve 1, Fig. 1 (also shown as curve 1 in Fig. 2 for comparison) after it had been heated to 765°C and chilled in water. This curve shows a pronounced exothermic effect which begins near 350° and causes the appearance of the heat absorption to be delayed until 540° is reached. Curve 5 was obtained on a sample of this chilled glass after it had been retreated by holding it for one hour at 520° and re-chilling it in air from this temperature. This curve shows no exothermic effect[1] below 500°C, but there is a slight indication of a double absorption region, as may be noted. It also resembles in many respects a large number of the curves obtained on original specimens collected from time to time. This resemblance would make it appear that the treatment given these specimens approximated the last treatment given this sample: *i. e.*, after being molded or blown they were probably cooled quite rapidly to an annealing temperature near 520°C, annealed for a short period, and then finally cooled again rather rapidly to room temperature.

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[1] The small rise in this curve near 600°C is undoubtedly due chiefly to a tendency to wipe out the abnormal temperature difference caused by the preceding endothermic effect, although some glasses have been found which seem to show two or more regions where exothermic effects may appear.

Curves 6, 7, 8 and 9 (Fig. 2), all of which have been practically duplicated by curves obtained on original specimens,[1] resulted from tests on other samples of this same chilled portion of the glass re-treated in much the same manner as the sample corresponding to curve 5: namely, after being heated for one hour at the indicated temperatures, 560°, 600°, 640°, and 680°C respectively, they were cooled rapidly in air. In curves 7, 8, and 9 the exothermic effect again becomes apparent and in the last of these it is almost as pronounced as it was before the re-treatment; consequently curve 9 differs very little from curve 4 in form. This similarity does not mean, however, that the re-treatment failed to remove the effect of the previous chilling in water, because other experiments have led to the conclusion that the effect of this first chilling was doubtless almost wholly removed before the glass reached 680° while reheating for the second treatment, and that the exothermic effect observed in curve 9 is undoubtedly due almost entirely to the air chilling in the latter treatment. This view is further substantiated by the almost identical forms of curves 9 and 10, since the latter was obtained on a sample of the original glass after it had been given only a single treatment duplicating the re-treatment given in securing the former.[2]

In Fig. 3, curves 11 and 12 (the latter resulting from a test taken immediately after that giving the former) are plotted together for the purpose of comparison, since curve 11 was obtained on a sample of the original glass while curve 12 was secured on a sample of the same glass specimen after being specially treated to bring out, if possible, the double absorption region more definitely. This special treatment consisted of holding the glass for an hour at about 700°C, cooling it at a rate of 20° per hour to 600°, then to 590° during the night and again at 20° per hour to 450°, where it was held over night before being cooled slowly to room temperature, and it produced, as the curve shows, the desired effect. Convenience played a considerable part in the choice of the above schedule, and undoubtedly treatments less elaborate can be devised to produce and even to enhance the effect obtained. No further attempts, however, of this kind were made, since this result, together with those of the preceding tests, seemed sufficient to substantiate the belief that the variety of effects observed with different specimens of high silica glasses are due chiefly to the treatments given the ware.

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[1] As used here "original specimens" refers to the samples "as received" and does not mean that all of them were taken from new ware, since many of them were from used articles, a fact which probably accounts for some of the variations observed on testing such specimens.

[2] These two curves are a good example of the closeness with which curves on specimens of a glass in the same condition can be duplicated if testing conditions, particularly the packing, are the same. On the other hand, curve 1, Fig. 1, and curve 11, Fig. 3, both obtained on samples from the same original specimen but with several days intervening between the tests, during which time the apparatus was in almost constant use causing unavoidable, though small, changes in the packing, etc., show some of the variations that may be caused by changing the testing conditions. The differences in the latter curves, although noticeable, are not extreme and consist chiefly of a change in the magnitude of the drop (500° to 580°C) and of the return (580° to 620°). Experience based on series of consecutive tests on samples from a single homogeneous specimen shows, however, that these variations are greater than they should be with homogeneous glass, if no changes had taken place in the testing conditions.

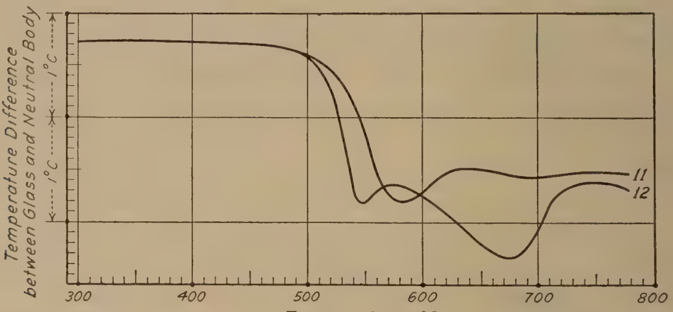

FIG. 3.

Curves for Window Glass

In Fig. 4 some curves for a commercial window glass are given to show the differences between the curves for high silica and ordinary glasses. Curve 13 obtained on an original specimen of this glass shows the form usually found for many of the ordinary window glasses procured on the market. A large sample of this specimen was more thoroughly annealed by holding it for 22 hours in the range 520° to 510°C and then cooling it at an increasing rate starting with about 10° per hour. Part of this sample was then retreated by heating it to 670° and chilling it in air. Curves 14 and 15 respectively were obtained on the annealed and chilled parts of the sample. The first shows a higher degree of annealing than is usually found in commercial glass, while the second shows a greater degree of chilling.

Curves for Other Glasses

In regard to the differences in the curves for the various types of glasses it will be noted that the indications of a heat absorption effect in these curves are much more distinct than in those for pyrex and that the effect is confined to a narrower range. Most other clear glasses used in containers, optical instruments, etc., when treated in the same way, give curves similar to those in Fig. 4 except that the heat absorption effects occur in widely different temperature ranges depending on the composition. Their curves are therefor simpler in form than those for pyrex. Thus, when any one of these glasses is treated in the various ways followed in obtaining the curves shown in Fig. 2, excepting, of course, that the treating temperature must be chosen in conformity with the region of the endothermic effect, complicated curves of the type found in that figure are not secured, but instead curves like those shown in Fig. 2, page 428, of the above mentioned article, "Certain Effects Produced by Chilling Glass," result. Under some treatments, however, certain peculiarities in curve form can be obtained even with these glasses. This happens when a chilled sample is treated for a short time at temperatures below the heat absorption region. Some curves for borosilicate and light barium crowns having the peculiarities here referred to were shown at the 1924 meeting[1] of the AMERICAN CERAMIC SOCIETY at Atlantic City. These peculiarities of curve form appearing when such glasses are so treated are insignificant in magnitude, however, relative to those found in the foregoing curves for the high silica glasses.

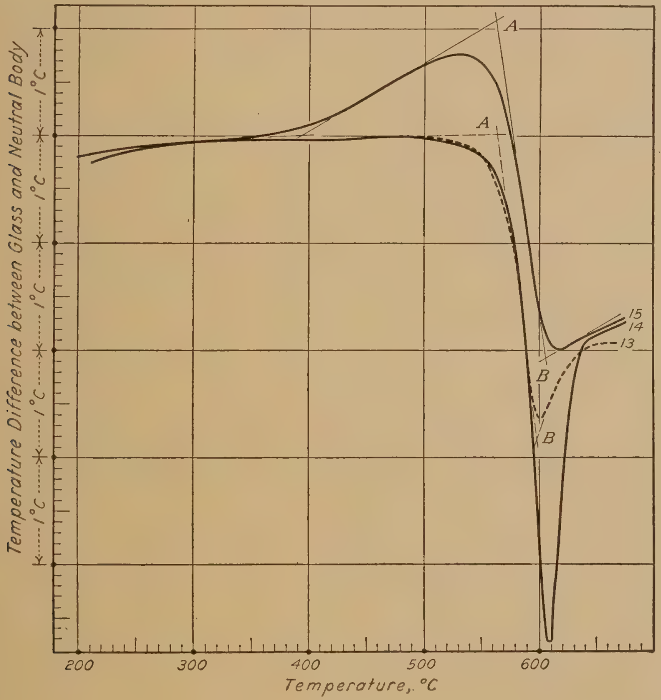

FIG. 4.

Comparison of Other Glass with Pyrex The greater width of the heat absorption range and the greater variety of curve forms obtainable with pyrex in comparison with the majority of glasses are probably due to no single cause. One of the properties of this glass, however, which may be related to, if it does not play a conspicuous part in these differences, is the slow rate at which its mobility increases with the temperature. An increase of about 12°C in temperature is required to double the mobility in the heat absorption range, whereas from 7° to 9° is sufficient for most ordinary glasses.[1] Though this value of Twyman's coefficient found for pyrex is not particularly large or exceptional, as the work of S. English[2] shows, yet it is undoubtedly enough larger than the average to suggest the possible presence of causes which may be responsible, in a measure at least, for some of the differences observed in the heating curves. Furthermore, if this coefficient should vary somewhat within a wide heat absorption range, it is possible that such variations indicate changes which might easily effect, or be related to, some of the diversities in the form of the heating curve resulting from treatment that may be found in that region. That the mobility and its variations should modify the heating curves seems more probable when it is considered that the transformations or readjustments producing the exothermic and endothermic effects are undoubtedly hampered by the rigidity, while they at the same time probably cause changes in it. This hampering of readjustments (as was shown in a previous paper)[3] may produce phenomena similar to the undercooling and superheating observed in substances which crystallize. Such retardations to readjustment would in all likelihood produce quite distinct indications of absorption and evolution effects in both the heating and cooling curves of glass when the temperature is rapidly changed. The same readjustment when proceeding to completion during a slow cooling would produce little more than what might appear to be slight changes in the specific heat.

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[1] The paper presented at that meeting is now being prepared for publication.

Another possibility which may influence the curve form is the presence of two or more types of adjustments or transformations which occur at their maximum rate in distinct temperature ranges. Such curves as No. 12 in Fig. 3 make this plausible. Granting, therefore, that different adjustments are possible in the same glass and that for their completion they require time, proper temperature conditions, etc., it may then be that some of these changes interfere with, or are necessary for, the completion of some of the others. Hence rapid cooling through, or long treatment within, certain temperature ranges may hinder, aid, or change completely adjustments which under proper conditions would occur in other ranges. The variety of heating curves obtained by altering the heat treatment of pyrex suggest this, and further, that the alterations in treatment should change the density, refractive index, durability (including solubility and resistance to chemicals), stability, etc. Such considerations point to the desirability of more thoroughly investigating those changes in the properties of glasses which may possibly be produced by such changes in treatment. In a ware like pyrex the properties in which these changes should be sought include its resistance to strain, mechanical shock and sudden changes in temperature; its resistance to chemicals and to deformation at moderately high temperatures, and also its density and expansivity.

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[1] No careful or extended measurements on the deformability of pyrex and its dependence on the temperature have been attempted in this laboratory, but the value given above is the result of some preliminary tests, which also indicated that its deformability around 550°C is not notably less than that for the majority of glasses showing heat absorptions near this point. Such glasses, however, usually lose their ability to sustain their own weight under standard conditions at much lower temperatures than the high silica glasses.

[2] S. English; *Jour. Soc. Glass Tech.*, **7**, 25 (1923).

[3] *Loc. cit.*

While it has been impossible so far to make any extended study involving these qualities, yet some preliminary observations on the density of pyrex indicate that it may be changed quite decidedly by altering the heat treatment. For example, nine samples of an original specimen of this glass, the form of whose heating curve indicated an initial condition between those existing when curves 7 and 8 in Fig. 2 were obtained, were variously treated by heating at least one of them at each of six chosen temperatures for different periods ranging from $1^1/_2$ hours at the highest temperature, 750°C, to about 64 hours at the lowest, 500°, before cooling them rapidly to room temperature. In every case the density[1] after treatment was increased, the greatest difference (0.0065) occurring for those samples treated at 500°, the least (practically zero) for the one treated at 550°. The average difference (0.0027) was about 0.12% of the average original density (2.2364, with a maximum deviation of 0.03% or 0.0007). Considering the unannealed condition of the original specimen this increase in density was to be expected in view of the results found on borosilicate crown.[2]

After this test the samples were again treated together for about three days near 600°C, and cooled as before. The densities after this second treatment when compared with the values obtained after the first were all decreased with one exception, that occurring in the case of the sample previously treated at 550°. The average density was now 2.2358, with a maximum deviation of 0.0010, which is practically the original density. These two tests indicate, therefore, that the density of this glass can be definitely changed by altering the heat treatment.

In addition to the above tests some fragments of a pyrex beaker whose original density was 2.2385 were treated for about two days at 650°C after which they were found to have a density of 2.2382, showing a negligible decrease in value. This slight change can be explained on the assumption that the original density was approximately that which would be obtained by annealing somewhat above 600°, but lower than would result from a long treatment near 500°. In view of the character of these results it has been deemed advisable, however, to elaborate the tests considerably before drawing any more definite conclusions.

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[1] This work on density was all done in collaboration with E. L. Peffer of the Capacity and Density Laboratories, of this Bureau.

[2] *Jour. Op. Soc. Amer. & Rev. Sci. Inst.*, **8**, 436 (1924).

Conclusions

In conclusion it can be said that the heating curves presented here for some of the high silica glasses show definitely great modifications when the heat treatments are changed. These curves also indicate that the modifications obtainable with such glasses greatly exceed in variety those with most ordinary glasses. It appears from the preceding discussion that this greater variety of curve forms procurable with the high silica glasses may be due to such causes as the slow rate with which their mobilities change with temperature, or the presence of two or more groups or types of readjustments or transformations occurring at their maximum rates in different temperature ranges, and also the possibility that the completion of certain of these readjustments aid or interfere in the advancement of others. Moreover, it is quite possible that these causes, if they exist, are due to the high silica content. At least such effects from heat treatment are probably brought about by the greater chance, under certain conditions of composition and temperature, for the formation of certain molecules or groups of molecules. The density changes previously described indicate, at any rate, some phenomenon involving a closer molecular packing or association under long continued heat treatments, particularly in certain temperature ranges, notably below the beginning of the heat absorption.

The formation of different complex molecules or groups of molecules, if such occurs, need not involve a mixture of substances of such a type as to cause opalescence, or other visible effects resulting from inhomogeneities; since it is not necessary that either the complexes themselves or the regions occupied by various clusters of them be so large that they are even of microscopic size in order to produce the results so far discussed. Even if the aggregations cause regions of structural inhomogeneity approaching a macroscopic order, but do not produce marked optical inhomogeneities, they may still remain undetectable. If, however, there be considerable variation at the same time in the optical properties between the different regions, particularly when these regions are relatively large, opalescence, color, or lack of transparency may be produced. If there be differences in the expansivity, permanent local strains somewhat similar to those often observed around small striae may result from cooling. If certain of these regions of inhomogeneity be due to the presence of an excess of gaseous or easily volatilized constituents, under certain conditions small bubbles may even result.

In regard to the character of such possible structures very little can be definitely said. They might consist of complex molecules formed through ordinary reactions between all or some of the simple components, or they might be built up by a transformation resembling a polymerization which may occur between similar molecules containing one or more of the simple components. Whatever be the character of these transformations, some elements of the resultant glass, in some cases at least, will have the nature of, or resemble, colloids somewhat, and others crystalloids. As to those having a possible colloidal nature it is undoubtedly true that in certain glasses some of the components form aggregates of such a character that this conception must be admitted as applicable. It is also undoubtedly true that some of the components of a normal glass are in such a condition that they will, under certain circumstances, diffuse and crystallize with relative ease, and hence may be thought of as more or less crystalloid in character. In general, however, it is questionable whether real glasses in their normal condition are ever crystalline or contain crystalline structures, because glasses having an appreciable number of such structures will certainly show some evidence of them and must therefore be classed as devitrified.

A reasonable view, therefore, of the nature of glass which is in accordance with common experience seems to be that glass consists of a great number of both simple and complex components, the latter being formed from the simpler original ones. Of these, the larger, heavier components whose unwieldiness reduces the mobility and which crystallize with difficulty, if at all, either because of their small tendency to do so or because of the inability of exactly similar molecules to assume the requisite proximity and orientation, constitute the colloidal elements. The smaller components which have a greater mobility and diffusivity and a stronger tendency to crystallize comprise the crystalloidal constituents. A stable glass, therefore, would be one so made up that a preponderance of the components are colloidal in nature.

In any case, it appears that as a working hypothesis the conception of a glass as composed of a number of relatively large complex structures surrounded by a magma of the simpler components, or, if the complex aggregates or molecules are sufficiently numerous, as consisting of a framework or skeleton so formed by them as actually to enclose the simpler components, is justifiable. In the multiplicity of possible glasses all gradations between these extremes are likely to be encountered depending on the composition, treatment, etc. Under some conditions and in some temperature ranges relatively rigid materials may be dispersed in, or enclose, others which have different elasticities, or which are much more deformable, or even almost liquid. In such cases what approaches, or appears to be, a two-phase condition may arise, corresponding to that described by Filon and Harris in their article on "The Di-Phasic Nature of Glass;"[1] and also under certain circumstances, corresponding possibly somewhat to the conditions found in celluloid and other materials of that type. One of the important inconsistencies which appears to exist between the view advanced here and the findings of the above authors is the absence in their case of an effect due to heat treatment, for it has been assumed here that certain heat treatments at least should change considerably the number or the relative proportions of the types of components. This should affect to some extent such apparent phase relations and probably the stress-optical coefficient. It is possible, however, that the re-treatment received by the glass in their experiment corresponded roughly to the original annealing process, in which case the resultant condition of the glass may have been practically that previous to this treatment. This could happen even though the glass after this re-treatment appeared to be somewhat "disannealed," as they describe it, since the state of equilibrium between the components is not of necessity affected in exactly the same manner as the stresses which result from cooling.

A result of greater import in practical glass-making which might arise if the complex aggregates formed a more or less rigid and extended cellular structure holding the more deformable components in its interstices is found in the possibility that in certain temperature ranges these aggregates, in forming and building up the structure, compress the more liquid or gaseous components which are released or not absorbed in the aggregates, causing them to diffuse outward and ultimately to collect in certain localities and possibly also on the free surfaces of the glass. These components which are in excess and ejected in this manner would undoubtedly be of the more soluble type; hence, if they should collect on the surface the apparent solubility of the glass would be greatly increased until they were removed.

These materials, if they are relatively simple in composition as assumed, should after becoming localized crystallize rather easily, possibly causing opacity.[2] If they reach the surface they would no doubt, under certain conditions, increase the tendency for the formation of crystals there whenever it is contaminated or otherwise mistreated. These effects from contamination, etc., have been observed by almost everyone working with glass and described by many investigators, for example, in the article by Y. Amenomiya on "The Devitrification Caused upon the Surface of Sheet Glass by Heat."[3] The possibility that these effects are enhanced by the release and ejection of elements normally within the glass seems sufficiently plausible to warrant its suggestion.

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[1] *Proc. Royal Soc. London,* **103,** 561 (1923).

[2] Such an effect may be involved in the case of those enamels and opals which are less transparent toward the interior, presumably because the cooling at the surface is more rapid.

[3] *Jour. Soc. Glass Tech.,* **6,** 231 (1922).

If these undesirable effects do arise in this manner, remedies may be obtained by the methods usual in any such case, *i. e.*, by correcting the composition so that there is no excess of components that can be ejected, or by so adjusting the heat treatment of the glass that little or none of the more mobile components are unincorporated in the complexes and practically none are forced or diffuse outward; or, finally, by removing the ejected materials from the surface by some chemical treatment. With the possibility just discussed, resistance to water or chemicals might often be reduced as a result of certain methods of annealing. However, if all the components are absorbed in the structure, or if only the less soluble are left in excess by the annealing, then the resistance of the glass to solvents may be expected to increase, since the association of the simple components into aggregates should ordinarily decrease the ease of their removal by solvent action.

Attention has been called above to the possibility that the changes in the condition of the glass as indicated by variations in the heating curve forms obtained after heat treatment, may involve a considerable change in many of its properties. These indications, together with the possibilities just discussed, appear sufficient to warrant a thorough investigation of the variations which may be produced in such properties as the refractive index and homogeneity of optical glass, the expansivity and constancy of volume of glass for volumetric purposes and the strength and solubility of chemical ware. It is believed that such investigations will show that these properties may be controlled to a considerable extent by the heat treatment, and that the nature of a desirable treatment will depend greatly on the composition of the glass and also on the quality whose enhancement is sought.

At any rate it has already been shown in one of the articles cited that the form of the heating curve obtained for any specimen may be used to determine the temperature at which the condition of the glass, as controlled by its composition and previous treatment, is relatively stable. That is, a temperature may be found at which a long heating will produce no change in the curve form or density although a heating at higher or lower temperatures for corresponding periods will cause such changes. To do this, an investigation of the curve forms obtained from many different heat treatments is necessary. Such an investigation also often makes it possible to determine approximately the procedure previously followed in annealing the specimen of glass.

For certain high silica glasses such determinations have been found difficult, although the results given here indicate that they are possible. They also indicate that an extended study of the heating curves should be helpful in any investigation of the changes of the properties of these glasses with heat treatment and also in determining whether the annealing given them is satisfactory. Thus, certain of the curve forms (curves 1, 5, and 11 for pyrex and curve 13 for window glass) shown here are similar to those obtained on these commercial wares when said to be reasonably annealed for the purposes intended. Also, experience appears to show that it is usually safe to conclude that any sample of either of these glasses will be nearly as well annealed as any other sample of the same glass which yields, when tested under similar conditions, a curve of approximately the same form. It has been assumed, therefore, that these samples giving the above curves are all about equally well annealed and correspond in their general condition to the product usually put on the market. This must be qualified, however, if the sizes of the ware or specimens are too dissimilar, because of a possible wide variation in the magnitude of the stresses set up while cooling.

Curves which show the effect of severe chilling (such as 4 and 15) are never obtained on samples from reasonably well annealed commercial ware. The majority of the curves showing such extreme variations in form have been found on wares which had been in use for some time or on specimens for which annealing had been considered unnecessary.

Summary

In the foregoing a discussion is given of certain variations in form found in the heating curves obtained from glass. These variations are due to changes in the endothermic and exothermic effects caused by different heat treatments.

It is shown that these differences in the curves are relatively simple for many glasses but somewhat more complicated for others, including some of those having a rather high silica content. The greater variations produced in the curves by altering the heat treatments for the latter glasses make it more difficult to reproduce any particular one of their possible curve forms, that is, to cause the desired readjustments in the condition of the glass. It is shown, however, that this is undoubtedly possible if sufficient data are collected.

Curves are given which show that some of these glasses have two or more regions of increased heat absorption, which, as the discussion shows, is one of the probable causes for the greater changes in the curve forms. Some or all of these endothermic and exothermic effects noted appear to arise in part from phenomena similar to those of superheating and undercooling as well as from a tendency for a large or excessive number of normal transformations to occur within a restricted temperature range.

It is shown that the densities of these glasses are altered by the heat treatment, or more specifically by the choice of the treating temperature and the length of the treatment. This is in accord with the view that glass when held at a given temperature approaches a condition of at least approximate stability which differs from that which would be attained at any other temperature.

An added discussion deals with the bearing that the changes in the curve form and in the density due to heat treatment, may have in throwing light on the possible nature and character of the processes involved in the formation of glass. The possibilities mentioned include the release and segregation of components during the cooling of the glass or while it is being annealed and otherwise treated. These effects may hasten devitrification or cause bubbles and other undesirable features, such as the collection on free surfaces of components having high solubilities and low melting points.

Attention is called to the fact that it may be possible through regulating the heat treatment to control to a greater extent than is usually attempted many of the properties of glass, among which are the solubility and resistance of chemical ware.

It also appears that frequent tests determining the form of the heating curves under carefully standardized conditions would be valuable in glass plant practice as a means of aiding in the regulation of these heat treatments and in checking the results obtained.

CASTING CONTROL[1]

By Albert C. Gerber

ABSTRACT

Casting bodies can be toned to a point of success by a proper manipulation of carefully chosen clays, with particular emphasis upon the china clays. A simple casting test will shed light on their individual casting properties. Regulation of casting salts and slip density, and the employment of grog in casting bodies offer means for a certain amount of control, but the preëminent qualifications of a good casting body are a balanced clay content and a correct ratio of clay content to non-plastics.

The purpose of this discussion is to describe the practical application of the solid casting process to sanitary ware.

Role of Ball Clays

Of those elements which make a good casting body, there is not one which exceeds in importance the proper proportioning of the clay. To have the ratio of clay to non-plastics correct is of course not enough. There must be painstaking care in the selection of clays employed, and the basis of selection should primarily be casting properties. Aside from impracticability in firing, it is well understood that any body containing only ball clay, irrespective of what the ratio of clay to non-plastics might be, would not adapt itself to successful casting. Ball clays to be sure contribute the very essential property of fluidity to a casting body, but the moment the mold has been filled, this most valuable property of ball clays, as far as casting is concerned, has largely played its part. The finely dispersed clay particles are rapidly floated toward the mold surface, upon which they build up with sufficient density to impede the passage of water from the center of the piece to the mold. Sections of uneven density result. It consequently becomes necessary to introduce into a casting body a tempering influence which will modify this behavior of ball clays. This is essentially the rôle of china clays.

The limits of these two generalizations are, however, extremely far apart, encompassing clays of widely different characters. Viscosimeter tests of ball clay slips will credit some ball clays with extraordinary fluidity, whereas others develop it only to a moderate degree. As a class, English ball clays are highly fluid, the dark clays generally more so than the light. There are Tennessee clays which practically match the English clays in this respect.

It is to be noted in this connection that a fixed addition of casting salts to different ball clays is hardly likely to operate advantageously with all of them. Due to their varying soluble salt contents, ball clays respond quite differently to given amounts of casting salts.

Amount of Ball Clay Required

As a rule the average sanitary ware body for pressing does not contain sufficient ball clay to cast well. It is certainly true that the character

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[1] Received Oct. 20, 1924.

and amount of the china clays used determine to a considerable degree the amount of ball clay needed, but only in exceptional cases can sanitary ware be cast with a ball clay content less than 14%. A reasonable maximum would be 20%. Also in many instances experience has proven the desirability of utilizing a blend of ball clays rather than a single clay. Likelihood of disturbance due to variations of quality of individual clays becomes correspondingly smaller, and by careful blending, smoother slip working properties can undoubtedly be attained.

Role of China Clays Whereas with ball clays the consideration of paramount importance is fluidity, with china clays this is of only secondary importance. It frequently happens that the results of viscosimeter tests of china clays which can be used interchangeably in casting bodies, differ most widely. From a casting standpoint the *sine qua non* with respect to china clays is proper behavior in a body *after* the molds have been filled.

Method of Test for Casting Behavior A very simple and useful test will illustrate. Tile casting molds measuring 3 x 6 x 1 inches with one-inch round plaster feeds in one end are required; also plaster funnels. Using the clay under test for the entire clay content, a 10-pound batch of test body is thoroughly mixed into a slip and dried on a plaster bat. To it is added a standard amount of salts (10 to 13 grams each of sodium carbonate and sodium silicate). The batch is then worked into a uniform casting slip of about twenty-nine ounces per pint depending somewhat on the clay, and poured into the molds, noting the time of filling. Using a blunt wire rod about $^3/_{16}$ inch in diameter, the funnel and feed hole are gently probed from time to time in order to determine within reasonable accuracy the time of feed shut-off. More than one tile should be cast, in order that final probing may be done in a mold which has not been previously disturbed. Also to be guarded against is nonuniformity of feed and mold condition. Results obtained in perfectly new molds can hardly be duplicated in a much older or in a wet mold.

Comparison of Clays Ball clays tested in this manner will register a clear open feed for as long as seven or eight hours. Some china clays on the other hand will close off in less than ten minutes, while others stretch out to an hour or slightly longer. To be observed also is the manner in which the tile has been formed, whether extremely hard and of accurate outline or whether the sides are hollowed and the center tending to be soft.

Some clays will scum the molds badly. Obviously, if a pure ball clay body remains open and soft-centered for a long time, one would naturally turn for correction to a clay permitting easy passage of water through the slip to the mold, one which shuts off quickly and packs solidly. Widely different clays accomplish this. Extremely gritty washed kaolins from the south Appalachian deposits will serve this purpose. This type of clay is of a low plasticity and develops almost no flow whatever. As a result, it produces a sluggish slip. Other undesirable properties are very inferior green strength and poor vitrification. For the purpose however of "quickening" a casting body, of facilitating drainage from the middle of heavy sections, these clays operate to splendid advantage.

Certain off-grade English china clays meet the same requirements. Differing from the Appalachian clays, these clays become quite plastic and develop fair fluidity with additional advantages of much superior green strength and improved vitrification. Despite the wide variance of their ordinary physical properties, these two types of clays have in common the property of quick action in molds and solid casting. There is one slight difference to be noted. Where the American clay is used, the safe working range of the body in the mold is likely to be short. Slight delay on the caster's part in taking down his molds is likely to result in cracks. Using the English clay, the need for exactness in timing molds is not quite so imperative.

Between these two broad groups of slow open casting and quick solid casting clays, is a group of clays which because of their mid-way properties lend themselves well to the regulation of casting bodies. Assuming that a given body dries so rapidly in the molds that workmen cannot dismantle quickly enough to avoid cracks, the substitution of certain plastic Georgia kaolins in proper amount will tone down the speed of drying to a point of greater safety. The casting test shows that this clay retains an open feed for about an hour. It can accordingly be utilized to excellent advantage as a retarder in bodies where mold behavior is too rapid for safety. Another group of clays which belong in this general class are the Florida kaolins. The casting action of the better grades of these clays is slow. It is to be noted, however, that the natural drying shrinkage of some of these clays is so great that oftentimes any casting advantage is more than offset by losses from excessive shrinkage.

Casting Behavior

The mold behavior of a casting body should be such that the workman is not compelled to work at great haste to keep pace with it. Under ordinary circumstances molds should be left up $2^1/_2$ to 3 hours. As the percentage of non-plastic material in a body exceeds 58 to 60% the likelihood of preparing a safe easy-working body, gradually diminishes. With a clay content as low as 40%, one may not only expect weakness in drying and firing, but anticipate casting difficulties as well. In some instances, bodies are so designed that pieces may remain in their molds six or seven hours before dismantling without injury to the piece. Where much ware of intricate design is being made, a very slow body has decided advantages in that it allows a wide margin of time for each operation. For ordinary ware, such practice is not strictly necessary, and may in fact invoke some hardship when unduly slow drying impedes production and compels the use of extra setters and extra floor space. Aside from the proper selection of clays, toughness in a casting body is generally a matter of *sufficient* clay content.

Use of Electrolytes It is of course well understood that manipulation of the salts used in preparing casting bodies offers a means of regulation. Soda ash and sodium silicate are the deflocculents in common use, and general practice is to use them together in equal amounts. Unfortunately owing to the different physical reactions of clays to these salts, generalizations on the extent to which a casting body can be controlled by this means are impossible. Some bodies require as low as twenty ounces each of soda ash and sodium silicate per 1000 pounds; others require double that amount. In a very general way, the greater the clay content the less the amount of salts required. Very frequently when a casting body sets up too rapidly, a reduction of casting salts will effect a remedy. What prevents broad statements in this direction is the well-known fact that a curve in which fluidity is plotted against gradually increased salts is not a straight line but a parabola.

Weight of Slip Very important in connection with the preparation of a casting body is the weight at which it is used. An added fraction of an ounce or less, oftentimes rectifies bad working properties. Again it becomes difficult to generalize, inasmuch as every body works best at its own peculiar weight. An average weight for ware of ordinary thickness would be 31$^1/_2$ ounces per pint. The water content of such slip approximates 23%. Where the thickness of ware exceeds $^5/_8$ inch it will be found advantageous to use heavier slip, up to a weight of 33 ounces per pint. The usual accompaniments of excessive salts are scumming of molds, difficulty in delivering pieces from their molds, crusting of the piece in the mold and a tendency toward "salt blisters" on the edges of ware from the kilns. Where the amount of salts used is insufficient, the slip will be dead and sluggish and the tendency in the molds will be to remain soft and not pack.

Use of Grog The use of grog offers a valuable means of regulating casting bodies. For example in the manufacture of heavy sinks and urinals, where the immediate problems are not only to fill the piece solidly, but to avoid drying and firing loss from undue shrinkage, the addition of from 20% to 35% of 30-mesh vitreous grog, depending on the extent of the original clay content, will be distinctly beneficial.

In a coarse grog body it becomes necessary to increase the amount of salts normally used, particularly sodium silicate.

Ground to the fineness of commercial ground materials, vitreous grog is an exceedingly useful ingredient in casting bodies. The extent to which it can be used depends again upon the clay content of the body in question. However, many bodies whose compositions do not readily lend themselves to casting, can be made to cast at most any desired rate of speed by the introduction of the proper amount of finely ground grog. The effect upon vitrification is very slight.

Correction of Slip Eliminating from discussion the very important considerations of mold design and mold condition, the suggestion is offered that initial effort to improve the casting qualities of a body begin with the weight of the slip. If pieces tend to crack in some particularly sensitive spot, both on the bench and from the kilns, perhaps a slightly heavier slip will slow up the casting process to a point of greater safety. As a second expedient, regulation of casting salts may bring about improvement. Where pieces remain in a soft unstable condition irrespective of a reasonable length of time in the mold, an increase in salts may be the answer. Where drying in molds is entirely too rapid and mold surfaces become badly scummed, improvement may follow reduction of salts. If neither nor both of these bring improvement, then undoubtedly there is need of toning the body composition one way or another as previously suggested.

Electric Porcelain & Mfg. Co.
Trenton, N. J.

A STUDY OF SLIPS FOR STANDARD FINISH TERRA COTTA (CONES 4-5)[1]

By H. E. Davis and J. S. Lathrop

ABSTRACT

The objects of the study were (1) to ascertain proportional limits of Cornwall stone, feldspar, flint and clays in terra cotta slips at cones 4–5, and (2) to evolve a slip that will be (*a*) highly vitreous, (*b*) white, (*c*) have a firing range which will not be affected by normal kiln variations and (*d*) freedom from crazing, checking, peeling and flaking. Compositions for various slips are given.

Objects

The objects of the present study are:

1. To ascertain proportional limits of Cornwall stone, feldspar, flint and clays in terra cotta slips at cones 4–5.
2. To evolve a slip that will be (*a*) vitreous to a high degree, (*b*) as white as possible, (*c*) sufficiently long firing range to be unaffected by normal kiln variation, (*d*) free from crazing, checking, peeling and flaking.
3. To note the effects arising from change of materials.

Work Reported by Others

Mr. Geijsbeek[2] notes that the use of flint is unsatisfactory, and, that a slip should have a shrinkage equal to or greater than the body to which it is applied, but never less.

R. T. Stull[3] brings out the following points of interest.

1. Cracking in the dry state is caused from too high a clay content, especially china clay. This is remedied by increasing non-plastic at the expense of clay, or by the addition of soluble material such as soda ash or borax.
2. Cracking in the fired slip may result from the same conditions, or from too high feldspar or Cornwall stone content.
3. Crazing is caused by too high content of flint, feldspar, or Cornwall stone; by firing a feldspar slip at too high a temperature, or a Cornwall stone slip at one too low.

In "Clay Glazes and Enamels,"[4] Henry Griffen mentions,

1. Flint tends to decrease shrinkage, stop cracking, and increase whiteness.
2. Cryolite at a given temperature produces a more vitreous slip than feldspar.
3. Ball clay tends to stop peeling, increase shrinkage and destroy whiteness.

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[1] Presented at the Summer Meeting, Los Angeles, Calif., Oct. 6, 1924.

[2] *Trans. Amer. Ceram. Soc.*, **4**, 48 (1902).

[3] *Trans. Amer. Ceram. Soc.*, **12**, 711–65 (1910).

[4] Chapters 6, 7, 8, 9, T. A. Randall, Publisher.

Present Investigation

Materials The materials used were Cornwall stone and Swedish feldspar, imported from Harrison & Sons, England; a feldspar and flint obtained locally, English china clay, English ball clay, an especially plastic ball clay, known as English ivory fat clay and commercial whiting.

Method of Procedure The work was divided into groups as follows:

1. A preliminary study to determine the safe limits of Cornwall stone, feldspar, clay and flint.

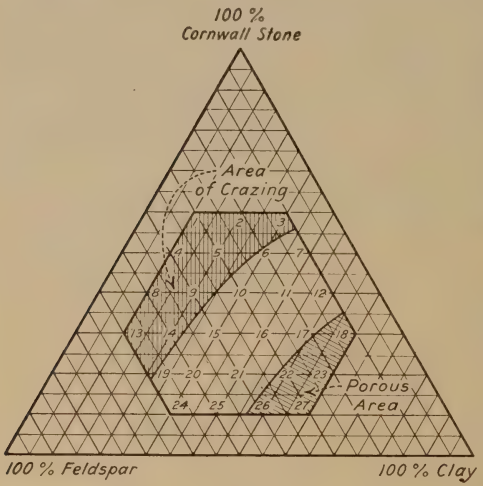

FIG. 1.

2. Two intermediate studies based upon the most satisfactory slip obtained in the preliminary work, to establish: (*a*) The use of whiting and flint over a closely confined range, (*b*) the finer limits of the use of Cornwall stone, feldspar and clay, and the proper proportions of china clay, ball clay and ivory fat clay.

3. A study of the effect of soda ash and borax.

The preliminary study was laid out as shown in Fig. 1. Ten per cent increments were used throughout, making in all a series of twenty-seven members. Flint was introduced by direct substitution in 10% increments, making groups A, B, C and D, having 0, 10, 20 and 30% flint, with 100, 90, 80 and 70% of the base field, respectively. In each group, the six corner members, Nos. 1, 3, 13, 18, 24 and 27 were wet ground, and the intermediate members blended. The feldspar content was made up of one-half Swedish and one-half local feldspar, and the clay content half and half English ball and china clays.

Results in Preliminary Study

The results obtained from this part of the work are indicated on the accompanying figures 1 2, 3 and 4 and may be briefly summarized as follows:

Crazing Crazing occurs in all group A members having less than 30% clay content, and extends to 40% clay where the Cornwall stone is highest. However, the crazing is more pronounced in the high feldspar area. The addition of flint in 10% increments pushes the crazing area farther and farther toward the maximum clay content, until in group D none is free except No. 27, having maximum clay and minimum Cornwall stone. Where no flint is included in the composition, crazing seems to go hand in hand with the overmatured, "greasy-looking," high feldspar slips, which is in accordance with Mr. Stull's remarks regarding overfiring slips high in feldspar. All slips low in clay and high in flux, either feldspar or stone, but more pronounced with feldspar, were apparently overmatured at cones 4–5.

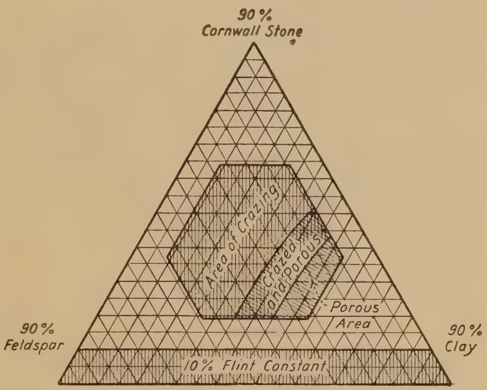

FIG. 2.

Crow's-footing Crow's-footing, or checking of the slips was much more in evidence in group A, in the absence of flint, than in the other groups, all of which seemed about the same in this respect, indicating that 10% of flint is evidently a sufficiently non-plastic addition to overcome largely this difficulty. As would be expected, this defect was more pronounced with increase in clay, but worse with any given clay content with high feldspar than with high Cornwall stone, due, no doubt, to the presence of a large percentage of free flint in the Cornwall stone.

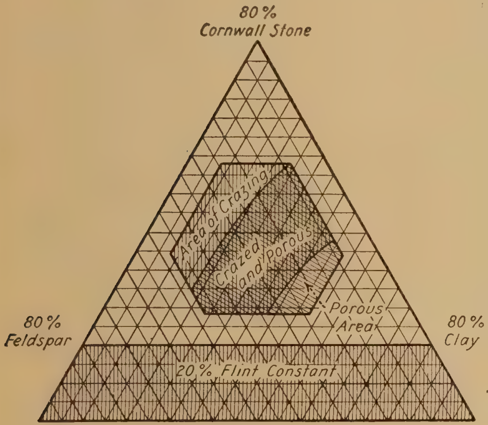

FIG. 3.

Color None were a good white. A certain degree of translucency in the high feldspar of Cornwall stone slips produced a pinkish buff; while with increasing clay content, the ball clay developed a pale cream.

Hardness Hardness or vitrification, was measured (also the crazing) by covering half the sample with writing ink, and washing off the unabsorbed. With no flint present, the vitreous, non-crazing area lay between the limits of 30% to 50% Cornwall stone, 10% to 30% feldspar and 30% to 50% clay. Below 30% clay and above 50% stone all slips are crazed. Above 30% clay and below 30%

stone, absorption was quite high. As little as 10% flint so increased the areas of crazing and immaturity that the two areas overlapped and left no area of satisfactory slips.

The best slip was No. 11 in group A (without flint). This slip was used as a basis for further study. Its composition is 40% Cornwall stone, 20% mixed feldspars and 40% mixed clays.

Composition Limits of Good Slips

The safe limits for vitreous, non-crazing slip are:

	Per cent
Cornwall stone	25 to 50
Feldspar	0 to 35
Clay	25 to 50
Flint	0 to 10 or less

Effect of Flint and Whiting

Number 11 group A was chosen as the base slip, having the following composition:

	Per cent
Cornwall stone	40
Local feldspar	10
Swedish feldspar	10
English ball clay	20
English china clay	20

Figure 5 shows the variation in whiting and flint.

Results

Whiting in any quantity up to 5% did not act as a flux, but rather as a refractory and a non-plastic, whitening the slip noticeably and apparently preventing crow's-footing. Flint up to 5% produced no crazing, and had no apparent effect other than to function as non-plastic and prevent crow's-footing the same as did the whiting.

As flint up to this amount is apparently beneficial, it was decided to use 3% in a slip for subsequent investigation. Knowing from past experience that whiting shortens the safe firing range, but with the present evidence of improved whiteness and decreased crow's-footing a similar addition of 3% was decided upon, making the base slip formula:

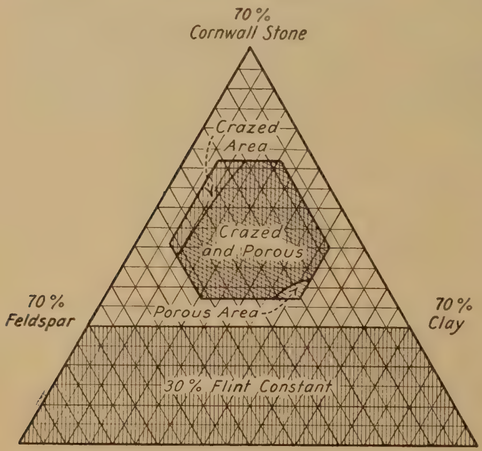

FIG. 4.

	Per cent
Cornwall stone	37.6
Local feldspar	9.4
Swedish feldspar	9.4
English ball clay	18.8
English china clay	18.8
Whiting	3.0
Flint	3.0

With this slip as a basis the percentage amounts of Cornwall stone, feldspar and clay were varied but no satisfactory slips were developed. The cause for this apparently was the use of even so little as 3% of whiting, again indicating the range-shortening effect of whiting.

The effects of variations in Cornwall stone, feldspar and clay were slight.

The effects of variations in the kinds of clay were more pronounced than those caused by other variations. Increasing china clay increases refractoriness and whiteness. English ivory fat clay lowers the refractoriness to a slight degree, but insufficiently to warrant its use when not readily obtainable.

The softening effect of Swedish feldspar is negligible.

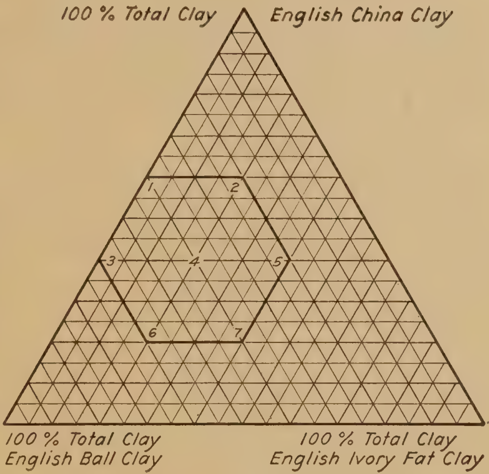

Fig. 5.

The slips containing neither flint nor whiting are all vitreous and free from crazing, being withal very good slips. The group containing 5% flint all show a strong tendency to craze.

No slips containing 2½% of flint and whiting were vitreous.

A good slip can be obtained with only feldspar, Cornwall stone and clays.

Soda and Borax

Borax up to 1% apparently had no effect and the only effect of the soda was electrolytic, reducing the water necessary for proper fluidity by 20% to 40%.

General Conclusions

Results in a vitreous slip for standard finish terra cotta at cones 4–5 were:

1. A low clay content causes crazing.
2. Too high clay content decreases vitrification, and only between the limits of 30% to 50% clay can good vitreous slips be obtained.

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3. Cornwall stone in quantities under 50% is beneficial. More than this amount produces crazing.

4. Good slips are obtainable with feldspar content up to 35% and perhaps higher.

5 Flint makes the slip more refractory and has a strong tendency to produce crazing.

6. Whiting even in very small amounts, decreases the firing range, and up to 5% acts as a refractory.

7. The addition of soda ash in the amount ordinarily used as an electrolytic has no apparent fluxing action.

No combination of materials was found which would produce a vitreous slip and at the same time a pure white one. No combination was found which would absolutely eliminate crow's-footing, but it is suggested that this might be overcome by different methods of spraying, or by the use of mica.

The proper proportioning of materials in the composition of a slip will, of course, vary considerably from place to place according to the different materials, the different body and different firing conditions, but the safe limits of composition of a satisfactory vitreous terra cotta slip at cones 4–5 will be as follows:

	Per cent
Cornwall stone	25 to 50
Feldspar	0 to 35
Clay	25 to 55
Flint	0 to 10 or less

Tropico Potteries, Inc.
Glendale, Calif.

A GENERAL THEORY OF SPALLING

By F. H. Norton[1]

ABSTRACT

A theory is proposed whereby certain physical properties of a material are combined in such a way as to give a measure of its resistance to rapid temperature changes. The important physical properties are the coefficient of expansion, the flexibility in shear and the diffusivity. These quantities have been measured for a number of types of refractories and the theory checked by actual spalling results on these same refractories. The theory applies mainly to a single brick free from external stresses.

Introduction

Spalling is a term applied to the fracture or disintegration of a material caused by rapid changes in temperature. Here the term will be applied only to fire brick. A typical spalling fracture on an exposed corner shows a more or less spherical surface, indicating that the isothermal plane has been followed. In other cases where spalling occurs on the face of the wall, a thin layer of brick of rather even thickness is separated. At times a brick under service conditions will be cracked squarely across approximately in the center, but whether or not this should be considered a spall is in some doubt.

The ability of a brick to resist spalling is extremely important in the majority of places where refractories are used. It has been said by those having much practical experience that by far the greatest cause of failure in refractories is spalling. Therefore a brick is often selected for use because of non-spalling properties, even though the other characteristics are not altogether satisfactory.

While there have been a number of investigations carried out to study spalling, about all that can be concluded from our present knowledge is that a good non-spalling brick should have;

1. A low coefficient of expansion.
2. A coarse structure.

Perhaps much of our confusion on the subject of spalling is due to the laboratory spalling tests failing to give results in accordance with practice. To heat a brick in a laboratory test to 2400°F when it is to be used at 2900°F can obviously give no satisfactory results. Again it seems probable that quenching a brick in water will not give the same results as cooling it in a stream of air. A really satisfactory laboratory spalling test is greatly needed.

It was felt that it might be possible to determine the spalling qualities of a brick by measuring separately all of the properties that affect spalling and then properly combine them into a single term. To do this it is necessary to analyze carefully the mechanism of spalling.

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[1] Babcock & Wilcox Fellow, Massachusetts Institute of Technology. Recd. Nov. 28, 1924.

Temperature Distribution in a Homogeneous Solid

Let us first assume that we have a solid with one limitless plane face. Originally this solid is uniform at temperature Θ_1, but at time t_0 the surface is suddenly cooled (it does not matter in what manner) to a temperature of Θ_2. What is the temperature distribution in the solid for different values of t?

To solve this problem it will be necessary to apply Fourier's equations of the heat flow.[1] As the surface is infinite the isothermal planes will be everywhere parallel to the surface of the solid. Putting $\Theta_0 = \Theta_1 - \Theta_2$, or simply shifting the temperature scale, the temperature Θ at any distance below the surface X and at any time t will be given by:

$$\Theta = \frac{2\Theta_0}{\sqrt{\pi}} \int_0^{\frac{X}{2h\sqrt{t}}} e^{-B^2} dB \qquad (1)$$

where h is a constant of the material. h^2 is known as the diffusivity of a material or the rate at which a point in a hot body will cool under definite surface conditions and is equivalent to $\left(\frac{k}{c\rho}\right)$, where k is the conductivity, ρ the density and c the specific heat per unit mass.

It should be noted that equation (1) is in the form of the probability integral and can therefore be readily evaluated from tables.

As will be shown later, the stress set up in a homogeneous material due to a change in temperature is proportional to the temperature gradient at any point. It will therefore be necessary to differentiate (1) with respect to X. First writing (1) as a function of the limits:

$$\Theta = \frac{2\Theta_0}{\sqrt{\pi}} \left[\phi\left(\frac{X}{2h\sqrt{t}}\right) - \phi\,(O)\right]$$

then

$$\frac{d\Theta}{dx} = -\frac{2\Theta_0}{\sqrt{\pi}} \left[e^{\frac{-x^2}{4h^2t}} \cdot \frac{1}{2h\sqrt{t}} - O\right]$$

$$= -\frac{\Theta_0}{h\sqrt{\pi t}} \cdot e^{\frac{-x^2}{4h^2t}} \qquad (2)$$

To show the practical application of this equation some curves have been plotted in Fig. 1 to give the temperature gradient ($h = .080$) when a body is cooled suddenly from 1500°F to room temperature. The gradient is of course highest at the surface but falls rapidly toward the interior. Near the surface the gradient falls rapidly with increasing time, but at a certain depth, the gradient increases with the time. This is one of the reasons why spalling does not usually take place immediately after the specimen is chilled.

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[1] Ingersoll and Zobel.

In an actual case the surface is not instantaneously cooled, first because a cooling medium cannot be instantaneously introduced, and secondly because perfect thermal contact cannot be made between the cooling medium and the surface of the brick. Equations (1) and (2) can be modified to take care of this effect as suggested by Ingersoll and Zobel, by adding a fictitious distance beyond the true surface. In this instance, however, as we are not interested in the region very close to the surface it will be more convenient to use a constant c to modify h.

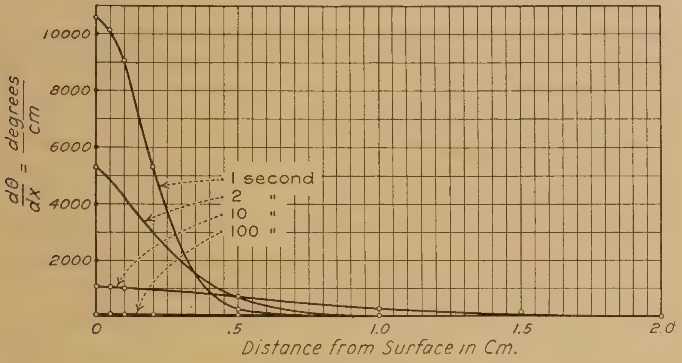

FIG. 1.

Only the case of an infinite plane surface has been considered. At the edge of a solid, the isothermal planes will not be parallel to the surface, but will be rounded off as in Fig. 2. This may be explained by considering that point A is cooled by the area abc in addition to the cooling received from an infinite surface such as a point at B. As the isothermals recede further from the surface the area abc increases and the corresponding departure from parallel conditions increases. The same conditions exist at a corner, except that the isothermal planes approach a spherical surface.

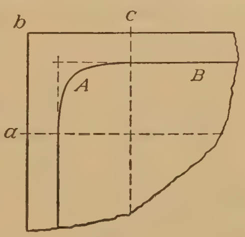

FIG. 2.

It is important to notice that the temperature gradient is slightly less at the edges and corners than on the faces of a cooling brick. Therefore the reason corners spall off is because of mechanical weakness rather than because of greater temperature gradients.

Temperature Stresses in a Homogeneous Elastic Solid

Spalling occurs almost universally along an isothermal plane. Therefore failure must be due to shearing, as it is inconceivable that any appreciable tension could occur under these conditions, if there are no external forces.

The assumption must also be made that a brick is an elastic, homogeneous medium. It will be shown later that a brick is almost perfectly elastic up to the breaking point. The homogeneity will depend on the process of manufacture.

The exact evaluation of the stresses in a brick under a given temperature distribution cannot be solved mathematically except in a few simple cases. However it is here only required to find the tendency to spall in terms of the physical properties of the material. That is, comparative but quantitative results are desired between various types of brick tested in the same manner.

Let us consider an isothermal plane *ab* in a portion of a cooling brick at a given instant of time. (Fig. 3.) Let the temperature of the plane *ab* be θ and that of another isothermal plane *dx* distant, $\theta + d\theta$, which gives the temperature gradient $\frac{d\theta}{dx}$. Let the plane *cd* cut the isothermal surfaces at a neutral point of shear.[1] Now measure along *ab*, a distance *s*, and erect the plane *ef*. If the temperature throughout the brick were θ this plane would be normal to *ab*, but under the existing conditions it will cut the $\theta + d\theta$ isothermal at a distance $s + s\,\Delta d\theta$ from *cd*. Δ is the coefficient of expansion.

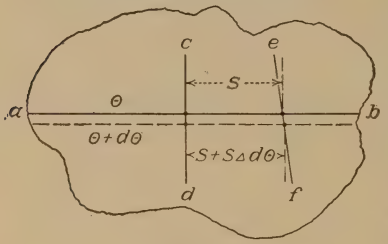

FIG. 3.

The shear strain is measured by the deflection of one plane in respect to another divided by the distance between them. In this case;

$$\phi = \frac{s\,\Delta\,d\theta}{dx} = s\,\Delta\,\frac{d\theta}{dx} \tag{3}$$

This means that the strain set up in a cooling body is proportional to the size, the coefficient of expansion and the temperature gradient. This explains why thick glassware cracks on cooling or heating more readily than thin ware. In large pieces of refractory ware, the temperature distribution may be so uneven that strict proportionality to *s* may well be doubted. This does not greatly concern us, for we shall compare specimens of the same shape and size and with the same temperature gradient.

The shearing stress at any point is;

$$f = \phi\,n \tag{4}$$

where *n* is the coefficient of rigidity.

---

[1] The neutral point will usually occur in a plane of symmetry in the brick.

From (2)
$$\frac{d\Theta}{dx} = \frac{c}{h}[1] \qquad (5)$$
vhere c is a constant.

Then the tendency to spall S is;

$$\frac{f}{f_1} = \frac{\phi n}{f_1} = \frac{S\Delta \frac{d\Theta}{dx} n}{f_1} = \frac{S\Delta \frac{c}{h} n}{f_1} \qquad (6)$$

vhere f_1 is the shearing strength.

But for brittle materials,

$$n = \frac{f_1}{\phi_1} \qquad (7)$$

vhere ϕ_1 is the maximum shearing strain.[2]

Therefore,

$$S = c\frac{s\,\Delta}{h\phi_1} \quad \text{or} \quad c_1\left(\frac{\Delta}{h\phi_1}\right) \quad S = \frac{\Delta}{h\phi} \qquad (8)$$

This shows that the spalling tendency of a brick is proportional to the oefficient of expansion divided by the square root of the diffusivity and he maximum shearing strain.

Departure of a Brick from a Homogeneous Material

The expression just developed for the spalling tendency applies only o a homogeneous material; a brick, however, may depart from this to a onsiderable extent.

In the first place there may be cracks and laminations, which, if they re in a region of high stress markedly increase the spalling tendency. uch laminations undoubtedly cause the cases of unusually rapid destrucion of a particular brick in a spalling test, but it is doubted that in general hey have much effect.

When the grain size of a brick is large, it would be considered far from omogeneous, but even in extreme cases the grain is small compared with he pieces lost in spalling.

When a brick is heated in service or for a spalling test, the surface is nuch hotter than other regions; so that there is apt to be a variation in he physical characteristics from place to place. This is especially true vhen the brick has not been fired as high as the temperature of use. In extreme cases the hotter regions of the brick may be softened and vitrified.

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[1] $\frac{d\Theta}{dx}$ is proportional to $\frac{1}{h}$ as small changes of h in the term $e\frac{-x^2}{4h^2t}$ have little effect hen t is reasonably large.

[2] The maximum shearing strain is the greatest distance a plane in the material can e moved parallel to another adjacent plane without rupture. The term flexibility ight also be used.

If a brick is considered as an elastic homogeneous medium, it would be thought under given changes of temperature that either spalling would take place at the first temperature change or no spalling would occur with an infinite number of changes. What actually happens however is a gradual loss of material. This may be explained by the fact that small flakes are lost each time and thus present new surfaces. Again cracks are started and gradually extend until they go across from surface to surface.

In order to determine how much the above causes of unevenness in the brick affect the agreement between the theoretical and actual spalling results, a number of brick have been carefully tested for physical properties and spalling.

The Maximum Shearing Strain, Stress and Coefficient of Rigidity of a Number of Fire Brick

In order to measure the characteristics of the brick as listed below, a number of 1 x 1 x 9 inch square bars were sawed out of each specimen. These bars were then cemented into holders and the angle and torque measured up to the breaking point. It would have been interesting to have had this test carried out to high temperatures, but the cost and difficulties would have been great, so a temperature of 500°C was used in each case.

Such a low temperature is justified because it has been noticed that in nearly every case spalling occurs at about red heat.

In all cases where the specimen was carefully held, there was no permanent set after removing the torque until a point was reached just before failure. That is the specimens all acted as if perfectly elastic.

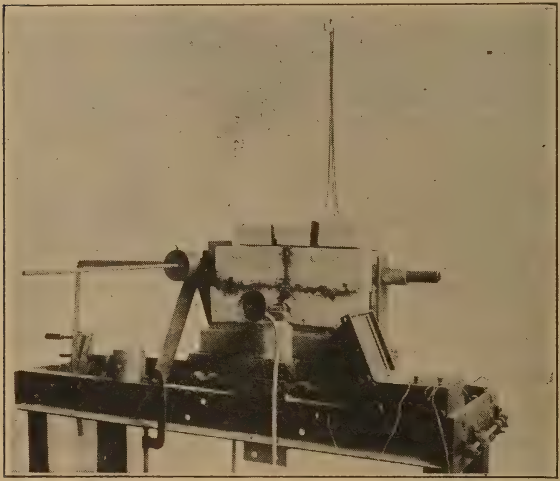

Fig. 4.

The apparatus used for these tests is shown in Fig. 4. A precision of about 2% was attained in all cases.

The brick tested are described in Table I below and represent a wide range. Some are experimental brick and others are extensively used.

TABLE I

Brand	Material	Grog	Bond	Hardness	Approximate burn. temp., °F	Remarks
A	Fire clay	Very coarse	Soft	Soft	2300	Commercial brick
B	Sillimanite	Medium	Little	Hard	3050	Special brick
C	Fire clay	Very coarse	Soft	Medium	2600	Same as *A* hard burn
D	Si C	20-mesh	Molasses	Hard	2800	Special brick
E	Fire clay	Coarse	Soft	Soft	2400	Commercial brick
F	Bauxite	Fine	Little	Hard	3100	Special brick
G	Fire clay	Medium	Soft	Soft	2400	Commercial brick
H	Kaolin	Medium	Little, hard	Very hard	3000	Commercial brick
I	Fire clay	Fine	Soft	Soft	2300	Commercial brick
J	Fire clay	Medium	Hard	Hard	2300	Commercial brick
K	Fire clay	Fine	Soft	Soft	2300	Commercial brick
L	Spinel	Medium	Hard	Hard	2500	Commercial brick
M	Silica	Fine	None	Hard	2700	Commercial brick
N	Same as *C* preheated to 2900					

The properties of the brick given in the table below are relative. The hearing strain is the angle through which the opposite faces of a one-inch ube are twisted. The shearing stress is the torque required to twist o this angle. The coefficient of rigidity is the ratio of the two.

TABLE II

Brand	Max. shear strain = ϕ	Max. shear stress, gm. cm.	Coefficient of rigidity
A	.114	45,000	400,000
B	.052	125,000	2,400,000
C	.050	44,000	880,000
D	.072	360,000	5,000,000
E	.057	63,000	1,100,000
F	.032	465,000	14,500,000
G	.090	37,000	410,000
H	.050	165,000	3,300,000
I	.107	64,000	1,070,000
J	.050	83,000	1,660,000
K	.089	70,000	790,000
L	.032	60,000	1,980,000
M	.094	160,000	1,700,000
N	.060	120,000	2,000,000

Each value is the average of a number of tests. Tests at 500°C.

The maximum shear strain varies between .032 and .114 or nearly four o one. The stress varies between 37,000 and 465,000, a ratio of 12. The igidity varies between 400,000 and 14,500,000, a ratio of 36 as the strongest rick have the least deflection as a rule.

It will be noted that brick *N* which is the same as *C*, but preheated to a igh temperature, shows a slightly increased flexibility and a greatly increased strength.

The Coefficient of Expansion of a Number of Fire Brick

A 1 x 1 x 9 inch specimen of each brick was placed in an electrically heated tube furnace and the expansion measured with micrometer telescopes. The coefficient in most cases was constant with change of temperature but the values given in Table III are for 500°C.

Table III

Brand	Coefficient of expansion (C) =	Brand	Coefficient of expansion (C) =
A	.0000051	*H*	.0000063
B	.0000039	*I*	.0000133
C	.0000050	*J*	.0000071
D	.0000031	*K*	.0000126
E	.0000053	*L*	.0000116
F	.0000037	*M*	.0000405
G	.0000104	*N*	.0000072

In general the brick highest in Al_2O_3 have the lowest coefficient of expansion, and those highest in SiO_2 the greatest. As an analysis of the brick is not available it is not possible to state whether there is a definite relation between the expansion coefficient and the composition. It is interesting to notice, however, that brick *N* which is the same as *C*, except preheated to a high temperature, shows a material increase in the coefficient of expansion. It is probable that brick heated high enough to combine all free silica will show a low coefficient of expansion.

The variation in coefficient of expansion between different fire brick is considerable and may account for discrepancies sometimes noted in wall expansions.

The Relative Diffusivity of a Number of Fire Brick

The value of the diffusivity can of course be obtained by measurements of thermal conductivity and specific heat. These measurements however take some length of time, so a method of measuring the relative diffusivity was devised.

A two-inch cube of the material was cemented up from four 1 x 1 x 2-inch blocks with a thermal junction at the center. This cube was suspended by the junction wires in an electric furnace until it had reached an even temperature of about 550°C; then it was taken out and suspended in a room free from drafts. The temperature of the center was recorded, and the slope of the cooling curve at 500°C was taken as the value for the diffusivity. This method is rapid and accurate where only relative values are desired.

The values for the specimens tested are given in Table IV below. The units are entirely arbitrary and the results are only comparative among themselves.

TABLE IV

Brand	Diffusivity = h^2	h	Brand	Diffusivity = h^2	h
A	38.2	6.2	*H*	40.4	6.4
B	42.6	6.5	*I*	39.2	6.3
C	39.6	6.3	*J*	36.6	6.0
D	67.2	8.2	*K*	37.8	6.2
E	42.3	6.5	*L*	41.1	6.4
F	38.7	6.2	*M*	44.4	6.7
G	38.9	6.2	*N*	36.8	6.1

Tests at 500°C

With the exception of the Si C specimen the value of h varies only a few per cent and is not usually an important factor in spalling.

Comparison between the Spalling Formula and Actual Tests

The results from laboratory spalling tests are available for the various specimens tested, and it was thought that a comparison between these results and the spalling formula would be interesting. This spalling test is somewhat different from the A.S.T.M. test in that the brick are heated each time to 2900°F and are cooled in a stream of air. A very careful comparison between this test and actual service has been made, and the agreement was found to be excellent. From five to ten brick of each kind were spalled and the average is given here.

Attention should be called to the two values given for brick *B* and *F*. These two brick both showed the regular type of spalling at the lower corners for several quenches, then suddenly the brick broke sharply across

TABLE V

Brand	ϕ		h	$(\Delta/\phi h)$	No. of quenches
A	.114	.0000051	6.2	72×10^{-7}	26.5
B	.052	.0000039	6.5	115	8.0
B	.052	.0000039	6.5	115	24.0
C	.050	.0000050	6.3	157	23.0
D	.072	.0000031	9.9	44	..[1]
E	.057	.0000053	6.5	143	15.6
F	.032	.0000037	6.2	110	2.0
F	.032	.0000037	7.3	159	15.0
G	.090	.0000104	6.2	187	12.2
H	.050	.0000063	6.4	197	10.6
I	.107	.0000133	6.3	197	8.4
J	.050	.0000071	6.0	237	5.2
K	.089	.0000126	6.2	229	2.7
L	.032	.0000116	6.4	567	2.4
M	.094	.0000405	6.7	644	.3
N	.060	.0000072	6.1	197	..

[1] No exactly comparable spalling value was available for this brick but it is undoubtedly lower than should be expected as an oxidizing atmosphere tends to convert the SiC into SiO_2 and thereby raise the coefficient of expansion.

near the center. The first value then gives the number of quenches until this break occurs and the second, the number, estimated from the amount lost at the tip, that it would have gone had the brick not broken in the center. This peculiar behavior needs further study.

If the value of $\frac{\Delta}{h\phi}$ is an index of the spalling tendency of a brick, as indicated by the theory, then these values plotted against the number of quenches for each specimen should fall along a curve rather than be widely scattered. Such a plot has been made in Fig. 5 and it is quite clear that the points group themselves into a definite band. The deviations that do occur can be explained by the fact that some of the brick were altered in heating from their original characteristics.

Specimen *K* which is considerably below the mean curve was noticeably laminated in structure. The higher values for brick *B* and *F* were only estimates.

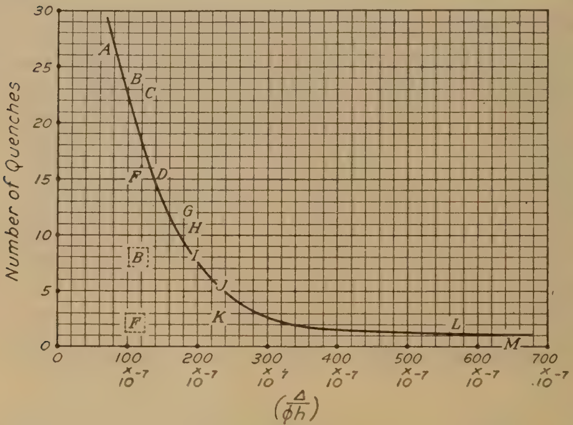

Fig. 5.

The form of the curve is of interest for it approaches a rectangular hyperbola asymptotic to the two zero axes. When the value of $\frac{\Delta}{\phi h}$ is high the brick show little difference in spalling resistance as they are almost completely shattered at the first temperature change. On the other hand the brick having a low value of $\frac{\Delta}{\phi h}$ increase rapidly in spalling resistance as $\frac{\Delta}{\phi h}$ is decreased. This behavior is not unexpected as it is simply an approach to a classification of brick into two sets, those that spall on the first quench and those that do not spall under an infinite number of quenches, as was previously discussed.

The best spalling brick of those tested withstood 26 quenches and had a value of $\frac{\Delta}{\phi h}$ of 72×10^{-7}. Suppose that by slightly increasing the flexibility or decreasing the coefficient of expansion a value of 50×10^{-7} were obtained, the brick should then withstand about 50 quenches. This illustrates the possibilities of making remarkable non-spalling brick.

On the whole it would seem that the theoretical work agrees with practice as closely as the nature of the tests will allow. While this new method cannot be recommended to replace the usual spalling tests without a more thorough trial, it is felt that more information is obtained as to the causes of spalling in a certain brick than by other methods.

Characteristics of a Good Spalling Brick

It is probably impossible to greatly vary the diffusivity of a brick and not destroy more important characteristics. The coefficient of expansion is dependent to a large extent on the material which oftentimes is fixed, but it seems probable that some change can be made by heat treatment and combination of free silica.

The flexibility of a brick, however, can be varied to a large extent by the manufacturer and it is here that efforts should be directed. A small increase in flexibility greatly increases the resistance to spalling. In general the most flexible brick are composed of rather large, hard grog particles held together with a soft porous bond. It is significant that the best non-spalling brick of the lot tested also had the greatest flexibility.

Conclusions

A theory of spalling has been developed which combines certain easily measured physical properties of a material to give a figure of merit which has been shown to agree well with actual spalling tests.

It is shown that a good spall-resisting brick should have (1) a high diffusivity, (2) a low coefficient of expansion, and (3) a high flexibility in shear.

This theory allows the study and development of spall-resisting brick on a scientific basis, but as yet only a beginning has been made on finding out how to vary the physical properties of the brick in the desired way.

In carrying this work on it would be interesting and valuable to determine:

1. The temperature distribution in a cooling brick by means of thermocouples fired into the clay and check these results with the theory.
2. The values of h, ϕ and Δ at all temperatures in order to find where $\frac{\Delta}{\phi h}$ is a maximum.
3 The effect of SiO_2 and Al_2O_3 content of a brick on the coefficient of expansion; also the effect of various firing temperatures and structures.
4. The effect of structure and firing temperature on the flexibility.

Acknowledgment

A large part of the experimental work carried out for this paper was done by Robert Richardson, at Massachusetts Institute of Technology.

THE CHANGES WHICH TAKE PLACE IN SILICA BRICK DURING THEIR USE IN OPEN-HEARTH FURNACES[1]

By W. J. Rees

ABSTRACT

A test on silica brick during their use in open-hearth furnaces is described. Four zones of varying characteristics in a silica brick are noted. A table presents the changes in composition and refractoriness which take place in brick used in basic and acid open-hearth furnaces. With highly converted brick, durability may be promoted indirectly by greater structural stability of the roof.

In the symposium on the "Selection of Refractories for the Open Hearth" conducted by D. A. Lyon,[2] reference was made by several speakers to the changes which take place in the structure of silica brick during their use. It was stated that when a roof brick which has glazed over, spalls, the freshly exposed surface fuses and drips. In this connection the following analysis and refractory test is of interest.

The appearance and structure of a silica brick which has been in use in an acid open-hearth furnace is shown in Fig. 1. At least four distinct zones may be distinguished: *A*, the end of the brick which has been exposed to the furnace. This zone is gray in color and the material has been more or less completely fused and it is by the flow of this layer that corrosion mainly takes place. It consists chiefly of cristobalite and magnetite. *B* is a black zone graduating into brown on its cooler end. Some traces of the original structure of the brick are visible, but the zone consists mainly of crystals of tridymite in a matrix of magnetite.

The contraction of zone *A* has caused the expulsion of the ferruginous slag into zone *B*. The silicates and alumina silicates of lime and alkalis, which have a lower viscosity, are carried in advance of this slag into zone *C* when a concentration of lime and alumina is found. This zone is usually brown in color, paling toward the cooler end. The increase in fuses reduces the refractories of this portion of the brick so that if, through defective management of the furnace, the brick becomes overheated fusion may occur. Rapid destruction of the brick may be caused by overheating it (such as by direct contact with a kiln flame) before it has become "seasoned" by impregnation with magnetite and the expulsion of the lime.

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[1] Received November, 1924.

[2] *Jour. Amer. Ceram. Soc.*, **7** [9], 705 (1924).

Note: (*a*) Complete penetration of hot end of brick by iron oxide. × 100.

(*b*) Skeletal crystals of cristobalite in glassy matrix. × 200.

(*c*) Large proportion of the quartz converted to twinned tridymite. × 50.

(*d*) Tridymite crystals, with residual quartz fragments surrounded by cristobalite. × 25.

(*e*) Fragments of unconverted quartz with cristobalite and tridymite in the matrix. × 25.

(*f*) This portion of the brick is practically unchanged. The fragments of ganister have unaltered cores. Tridymite and some cristobalite in matrix. × 25.

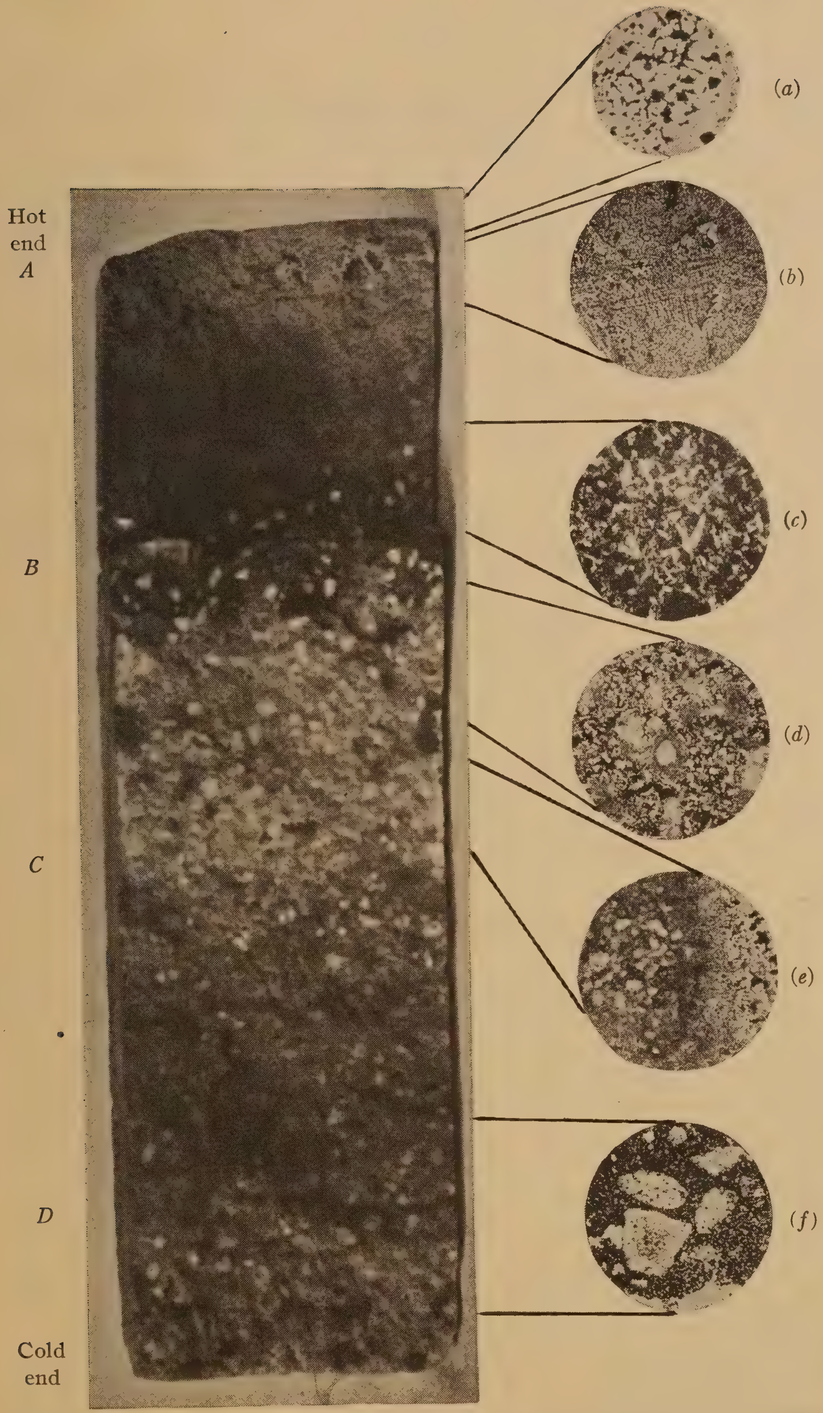

FIG. 1.—Vertical section and photomicrographs of silica brick from roof of open-hearth furnace. (See Note, page 40, for further description.)

Zone *D* is unchanged brick. Under normal circumstances it does not become hot enough for changes to occur.

The exact extent of these zones is a function of the temperature gradient through the brick. Changes of a similar character may be observed in brick which have been in use in a basic open-hearth furnace. The following table shows the changes in composition and refractoriness which take place.

BRICK FROM ROOF OF ACID OPEN-HEARTH FURNACE[1]

Zone	Structure	SiO_2	Fe_2O_3	FeO	Al_2O_3	CaO	MgO	Mn_3O_4	Refractoriness Cone
A	Cristobalite	79.6	13.6	5.7	0.8	0.1	....	0.3	33
B	Tridymite	74.8	19.0	4.4	1.1	.3	....	.2	33
C	Transition	91.0	2.5	...	2.7	3.4	0.05	.2	28
D	Unaltered	95.4	1.3	...	1.0	1.8	....	.1	32

BRICK FROM ROOF OF BASIC OPEN-HEARTH FURNACE[1]

Zone	Structure	SiO_2	Fe_2O_3	FeO	Al_2O_3	CaO	MgO	Mn_2O_3	Refractoriness Cone
A	Cristobalite	88.5	5.2	1.3	0.6	2.7	0.4	1.1	30
B	Tridymite	87.2	6.8	0.9	.8	2.8	.4	1.0	31
C	Transition	88.6	3.0	...	2.9	4.8	.3	0.3	27
D	Unaltered	96.2	0.9	...	1.1	1.5	.1	.1	32

It is apparent from these analyses and refractory tests that if the portion of the brick represented by zones *A* and *B* spalls away, the freshly exposed portion represented by zone *C* will quickly fuse and drip.

Two properties of silica which favorably affect the behavior of silica refractories in high temperature furnaces are (*a*) melts derived from silica have a high viscosity and there is consequently a definite tendency for the formation of a protective fluid or semifluid layer. (*b*) The flatness of the melting point curve of silica is such that at high temperatures, even in the presence of a good deal of impurity, much of the silica remains solid.

There has been from time to time a good deal of discussion as to the advantage or otherwise of high quartz conversion in promoting the durability of silica brick in the open-hearth furnaces. H. H. Thomas[2] has suggested that the actual density-concentration of silica is of more importance than the crystalline form in which it is present. There is something to be said in support of this view, but my own experience is that both high quartz conversion and high silica concentration are desirable if maximum durability is to be obtained. With highly converted brick durability may also be promoted indirectly by the greater structural stability of the roof as alterations in contour from excessive after-expansion may adversely affect the economies of the furnace.

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[1] (See also J. E. Stead, *Trans. Ceram. Soc.* (Eng.), **18,** Pt. 2; C. S. Graham, *Trans. Ceram. Soc.* (Eng.), **18,** Pt. 2.

[2] *Geol. Survey,* Spec. Reports, **16.**

ADAPTATION OF TUNNEL AND CAR KILNS TO FIRING REFRACTORIES[1]

By Philip Dressler

ABSTRACT

The success of tunnel kilns in a given industry is largely determined by the choice of the type best suited to the requirements of that industry. This paper discusses the adaptation of the various types of tunnel kilns to firing glass house refractories, clay, fire brick and silica brick.

Introduction

The report of the Committee of the Refractories Manufacturers Association on tunnel kilns[2] cleared up points of doubt regarding the success of tunnel kilns for firing refractories. There are tunnel kilns in this country firing satisfactorily and uninterruptedly at the highest temperatures required by the industry and on materials offering in many respects more serious firing difficulties than the great majority of refractory products. There are kilns firing tonnages of clay products of the same sort as refractories.

Tunnel kilns have demonstrated (*a*) a fuel saving of from 50 to 70% over intermittent kiln firing practice; (*b*) a saving of labor due to the better working conditions and the localization of the setting and drawing operations; (*c*) an increase in proportion of No. 1 grade ware due to better control at all stages of the fire and the ability to fire to higher temperatures without kiln marking on account of uniformity of burn and the low setting height of the ware; (*d*) shortening of the time required for firing, leading to a marked reduction in the quantity of material in process of manufacture and to the ability to fill orders for special material rapidly.

As pointed out by the Committee, there are a large number of tunnel kilns in Europe firing refractories. The reason they have not been employed more largely in America is that tunnel kiln designers have not sufficiently appreciated the variety of problems presented by the different kinds of refractories and have attempted to apply without modification kilns which have proved satisfactory in other lines, and under different conditions, to the refractory field. To be successful tunnel kilns must be designed and adapted to meet the conditions offered by the different divisions of this industry.

The Problems Peculiar to Firing Refractories

Generally speaking, from the standpoint of the tunnel kiln designers the refractories industry can be divided into three main sections:

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[1] Presented at the Atlantic City Meeting, Feb., 1924 (Refractories Division). Recd. Oct. 1, 1924.

[2] Preliminary report of the Committee on Fuel Conservation on the Railroad Tunnel Kiln, *Jour. Amer. Ceram. Soc.*, **5** [9], 602 (1922); A. F. Greaves-Walker and S. M. Kier, "The Suitability of the Tunnel Kiln for Burning Refractories," *Jour. Amer. Ceram. Soc.*, **6** [8], 891 (1923).

(1) Heavy and large special fire clay refractory shapes such as are used chiefly in the glass industry.

(2) Ordinary fire clay fire brick firing at temperatures not to exceed cones 14 to 16 and usually considerably lower, capable of being fired on a relatively short cycle and presenting no great firing problems.

(3) High fire refractories requiring temperatures of cone 18 and up and necessitating long periods of heat treatment to bring about complex mineralogical changes both in the firing and in the cooling, for instance silica, magnesite, chrome and other special materials.

Heavy Shapes On account of the difficulty of manufacture, length of time required for drying, high cost and other such factors, the usual plant manufacturing glass house refractories does not produce a tonnage to exceed thirty tons per day. This field, therefore, offers no great tonnage problem to the tunnel kiln designer. What is required to produce perfect results is an exceedingly steady, slow and controlled heating combined with a period of uniform temperature sufficiently long to give complete penetration to the center of individual pieces which in some cases may weigh as much as 2500 to 3500 pounds each. It is apparent that any rapid change of temperature at any point whether in the heating or cooling is bound to affect the outside of such pieces without affecting the inside and, therefore, to set up heavy strains. A sudden flash of heat in the high temperature region where vitrification is starting is quite sufficient to cause shrinkage and cracking of the outside layers over the inner core.

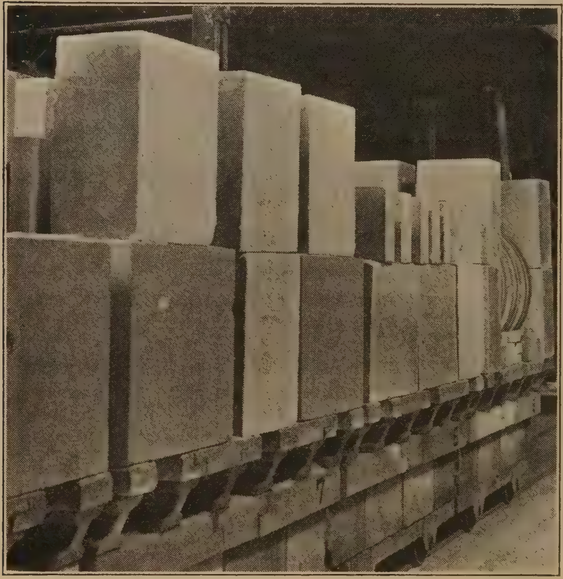

FIG. 1.

The kiln to meet the required conditions must provide the most gentle heating and cooling and the easiest control in all stages. In the opinion of the writer the muffle type of kiln is the one which most successfully can meet these requirements.

Muffle tunnel kilns are in use in this country for the firing of glass house refractories. The Committee has described the one at the Ohio Valley Clay Company. It has now been in operation for six years. Figure 1 shows the kind of ware fired in this kiln. Several others have been installed by the glass industry for preheating the heavy pots which in some cases are as much as four feet six inches wide, by six feet long, by forty-five inches high, weighing 3850 pounds and having thicknesses up to ten inches. These units have all been highly satisfactory and it does not appear that any other firing method can equal the results obtained. Figure 2 illustrates the entrance end of a pot arching kiln and Fig. 3 a pot being withdrawn at the hot end at 1800°F.

Fire Clay Brick The direct fire kiln with longitudinal draft, in which the gases of combustion are drawn from the fire boxes, at about the center of the kiln, toward the offtake ports at the entrance of the kiln, is best adapted to firing this class of ware both on account of cheapness of installation and simplicity of design. The chief problem in the past has been to provide a kiln which will handle sufficient tonnage. It is possible to design a kiln to produce up to 25,000 or 30,000 nine-inch equivalents or approximately 100 tons per 24 hours. To fire on a 72-hour cycle, such a kiln needs to be about 350 feet long. The earlier difficulties experienced by the designers in obtaining an even heat distribution in the high heat zones of this type of kiln, have been largely overcome by the more refined methods of burning the fuel and introducing the products of combustion into the kiln chamber. The practical size for the kiln car is one which carries six headers in the width and is loaded fifteen courses high giving about 1500 brick per car six feet long. The method of loading is shown in Fig. 4.

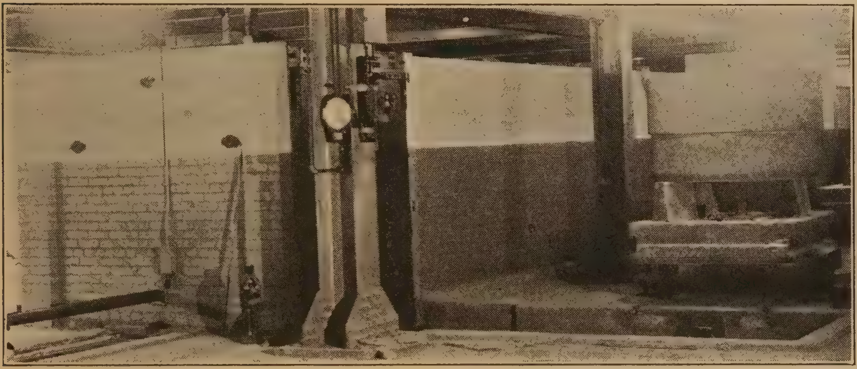

FIG. 2.

Kilns of this type have been built in this country from time to time, some of which have been more successful than others and some have been failures. Difficulties of operation experienced have been largely due to an inherent problem in this type of kiln to secure a good distribution of gases through the ware in the earlier stages of heating. The natural tendency of the gases is to pass through the space between the top of the ware and the crown of the kiln. When the gases reach the vicinity of the draft points they flow practically entirely in the space between the ware and the walls. This space cannot be avoided. There must be ample clearance everywhere to prevent a loose brick or poor setting from causing a wreck and these spaces are as a rule increased by the natural shrinkage of the material.

Fire clay goods offer a problem not presented by saggered ware in which the space occupied by the ware is constant throughout the length of the kiln. The result of the tendency of the gases to pass between the load and the kiln walls is that the center bottoms are not heated up satisfactorily in the early stages. As a rule such a kiln presents two very different heat curves for the top and the center bottom of the car. The top of the car follows approximately the heat curve of the crown of the kiln. The bottom lags far behind until when it comes opposite the first fire boxes its temperature is suddenly and rapidly raised. Due to the coldness of the bottom center brick in the preheating zone of the kiln there is a tendency to condense water vapor upon themselves which in some cases, especially of dry press brick, has led to serious slumping problems. These same brick, when they reach the first fire boxes then tend to have their temperatures raised so rapidly that they are cracked.

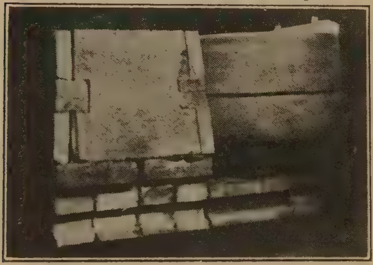

FIG. 3.

Many expedients have been adopted by tunnel kiln users to combat this. To close the space above the top of the ware as close as possible some have added baffles hanging from the arch, others have used baffles set upon the top of the ware to conform to the shape of the arch. The kilns designed by M. Faugeron, the parent type of today's direct fire kiln, were provided with recesses in the side walls with narrow points opposite each other on the two sides of the kiln, the object being to cause the gases to wind in and out of the recesses and give them a direction towards the center of the car. In other designs these recesses have been staggered with respect to each other, the idea being to cause the gases to follow a serpentine path through the preheating section of the kiln. It does not appear, however, that any of these recesses can prove very effective in accomplishing their object. Space must be left between the cars, the roof and the side walls. Gases in motion have momentum and under the influence of the suction at the entrance end of the kiln, a purely negative influence such as is produced by the devices mentioned above will not cause them to be deflected to any appreciable extent from the most direct path from the center to the entrance end of the kiln. Their mass and their momentum are too great. To change the direction of the gas stream a positive force is required.

In a recent installation of a direct fire tunnel kiln of the longitudinal draft type such a force has been applied so as to cause an even heating of the ware in the preheating zone by a positive circulation of gases through the lower part of the cars. This has been achieved by the application of the principle of draft reversal. The offtake flues on the two sides of the kiln are connected independently to the source of draft whether fan or stack. The draft is applied alternately to these flues so that for one interval all the draft is on the right hand side and for another interval is on the left hand side. (See Fig. 5.) In the construction of the kiln provision is made to prevent gases from passing from one side to the other over the top of the ware. (See Fig. 6.) At each reversal then in finding their way from the space between the ware and kiln, down which they normally travel, to the draft ports, on the opposite side, half the gases are obliged to pass through the ware from one side to the other. There are, of course, an infinite number of ways of bringing about this draft reversal. In this particular case, as illustrated in the accompanying photograph (Fig. 7) the reversing gear is driven directly from the coupling on the fan drive through a system of belts and reducing gears and is so arranged that the full draft is on each side for eight minutes and two minutes is consumed in changing from one side to the other. It is felt that this device offers a very simple solution of what has heretofore been a baffling problem in the design of this type of kiln.

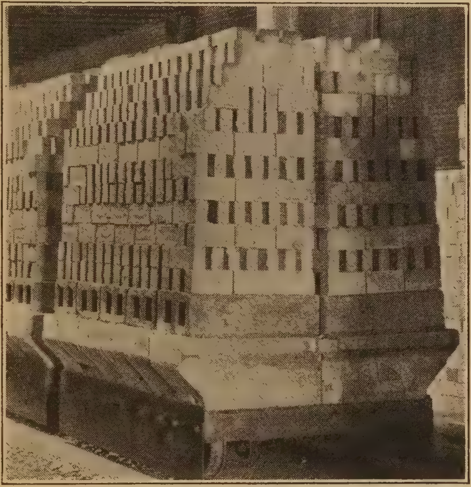

Fig. 4.

High Fire Refractories, Silica Brick and Allied Products

Apart from the high maturing temperature and the danger of cracking at all stages the main problem to be solved in firing silica brick and applied products in tunnel kilns is to obtain sufficient production from a kiln of reasonable length. J. Spotts McDowell has stated to the writer that in his opinion a firing cycle of 120 hours is the shortest one on which silica brick of American

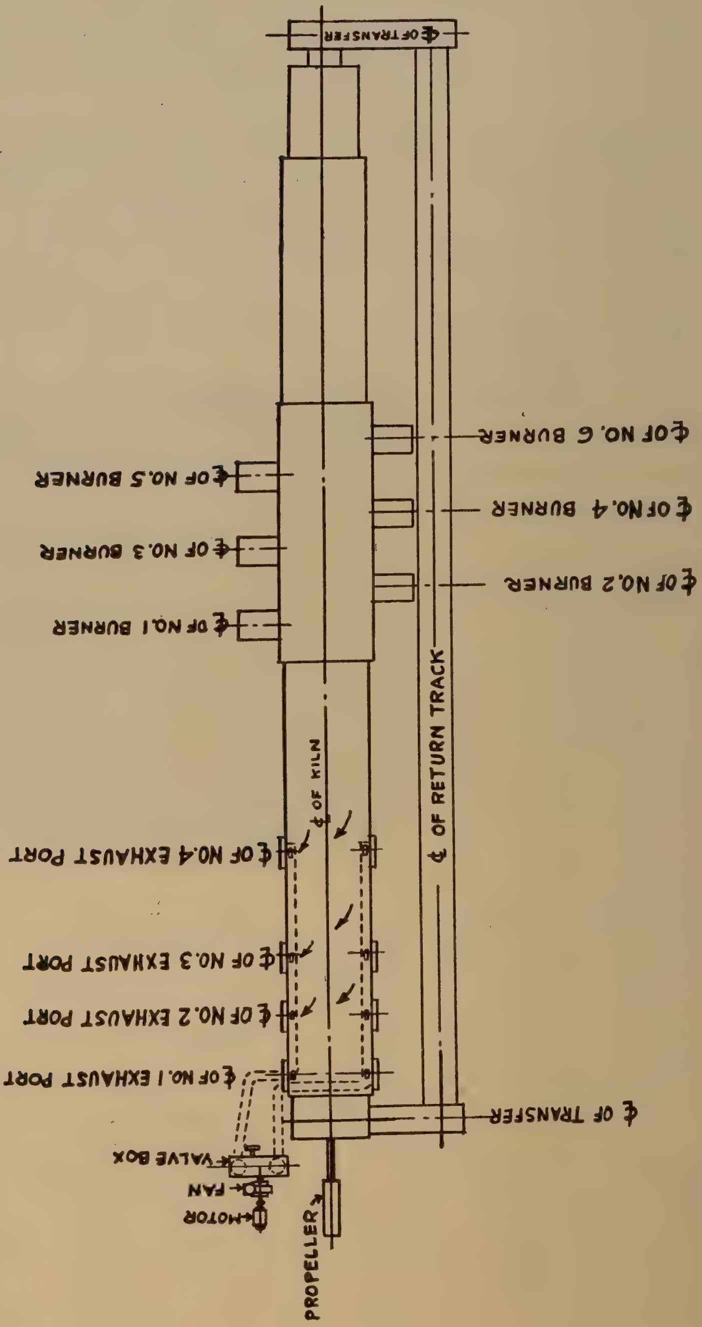
℄ OF TRANSFER
℄ OF NO. 6 BURNER
℄ OF NO. 5 BURNER
℄ OF NO. 4 BURNER
℄ OF NO. 3 BURNER
℄ OF NO. 2 BURNER
℄ OF NO. 1 BURNER
℄ OF RETURN TRACK
℄ OF KILN
℄ OF NO. 4 EXHAUST PORT
℄ OF NO. 3 EXHAUST PORT
℄ OF NO. 2 EXHAUST PORT
℄ OF NO. 1 EXHAUST PORT
℄ OF TRANSFER
VALVE BOX
FAN
MOTOR
PROPELLER

FIG. 5.

manufacture can be properly burned and on this cycle to obtain complete inversion a temperature of 1475°C must be maintained for eighteen (18) hours.

The longitudinal draft direct fire kiln described in the preceding section is very distinctly limited in width due to the difficulty in obtaining even conditions from side to center, not only in the firing zone but in the heating up and cooling off sections. Silica brick are very sensitive to cracking in these periods and unless a very even temperature condition can be maintained over the full cross-section at all stages, the firing cycle must be still further lengthened in order to insure that the material in the worst position receives the proper treatment, thus making the problem of adapting the tunnel still greater.

Since a car carrying six headers in the width is about the limit of what is practical in this type of kiln and assuming the minimum cycle of 120 hours, a very long kiln would be required to fire a satisfying tonnage of silica brick. In the report of the Refractories Committee, lengths of from five hundred to seven hundred feet for this type of kiln are mentioned. Such lengths do not appear to be practical. Few plants have sufficient space available for them and the distance through which the cars have to be moved both in the kiln and on the return tracks appear too considerable for practical, economical operation. What is required is a kiln which will permit of a much greater cross-section and which will hold many more brick to the foot run and yet permit an even heat distribution and the necessary control of the heating and cooling curves. In the opinion of the writer this can be achieved by the use of the Cross Fire Regenerative Kiln mentioned in the report of the Refractories Committee. Since no account of this kiln has appeared in the available literature, it may be of interest to describe it here.

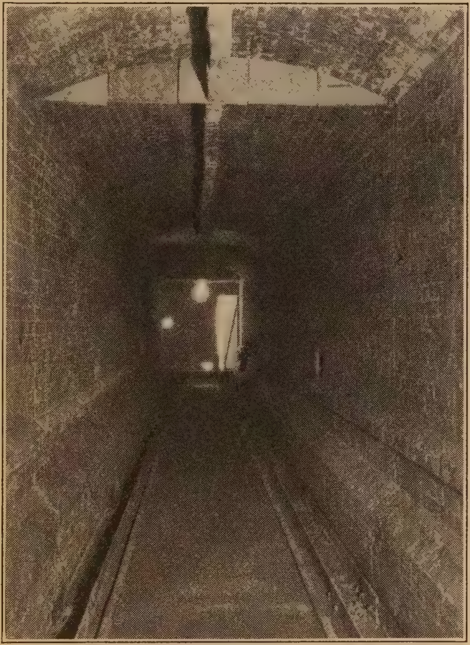
FIG. 6.

In this type of kiln, the gases, instead of being drawn longitudinally from the center toward the entrance end, pass transversely across from side to side. Two advantages arise from this—(*a*) the heating medium only traverses one zone and it is, therefore, possible to regulate each section of "heating up" and "furnace zone" independently of every other one. This manifestly is not possible where all the gases are drawn from the center toward the end. (*b*) Since the passage of the gases is transversely across the kiln they are compelled to pass through the centers of the cars and can not merely find their way longitudinally between the walls and the ware. For this reason cars of a much greater width can be used.

These results are achieved by using a multiplicity of burners on the two sides of the kiln, which are used alternately, the draft being switched from side to side at intervals. The sensible heat of the gases of combustion under these conditions cannot be used to preheat the ware, as in the longitudinal draft kiln, but instead is stored in regenerator chambers filled with checker brick and is recovered by preheating the air and the fuel when the direction of flow is reversed.

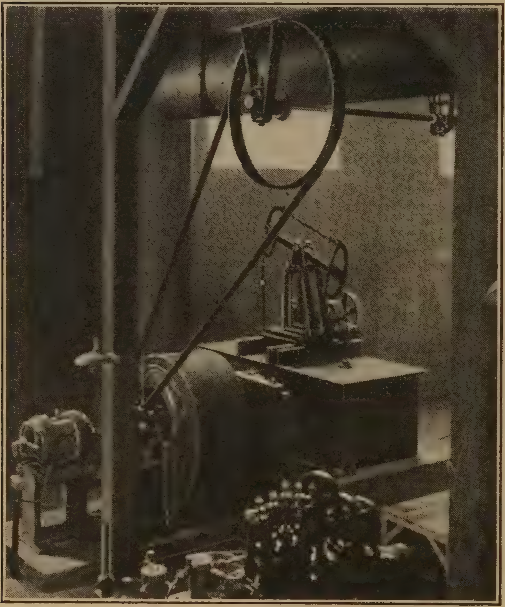

FIG. 7.

The problem of distributing fuel through a number of ports spread over a considerable length has fortunately been very thoroughly worked out in the design of by-product coke ovens and it has been possible to adapt the methods of the coke oven constructors very closely to the tunnel kiln.

The kiln from end to end is divided into a number of short sections, about 12′ 6″ long, each of which has its own independently regulated fuel and air supply and is operated strictly independently of the other sections. Such a kiln can be built in two different ways.

(*a*) With two trains of cars passing through in opposite directions, so arranged that the heat retained by the ware leaving the furnace zone is imparted to the ware entering it.

(*b*) With a single train of cars. In this case the heat of the ware leaving the furnace zone cannot be applied satisfactorily to the preheating zone but can be conveniently recovered as hot air and used for other purposes.

Figure 8 illustrates diagrammatically a kiln of the former type with two trains of cars, as adapted for firing silica brick.

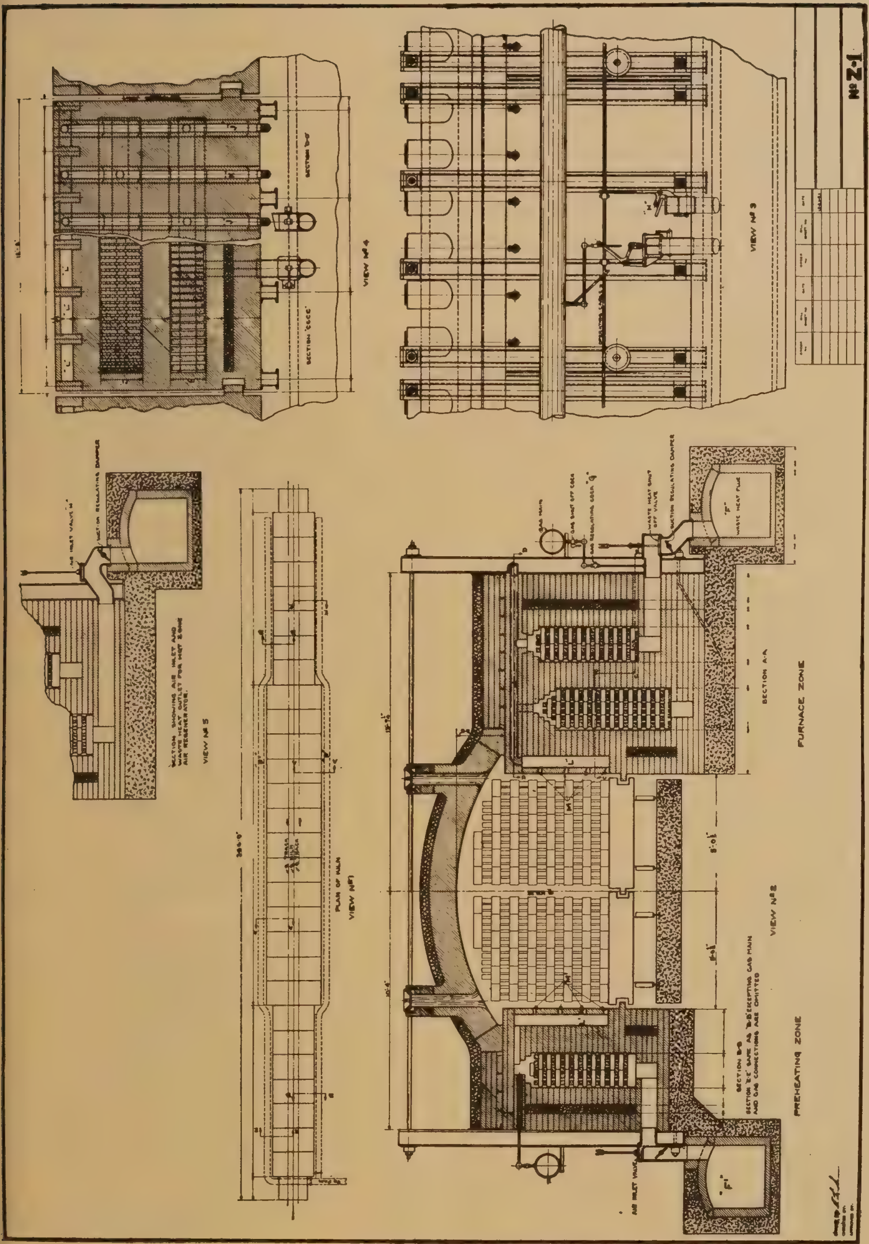
№ Z-1
VIEW № 1
PLAN OF KILN
VIEW № 2
VIEW № 3
VIEW № 4
VIEW № 5
SECTION SHOWING AIR INLET AND WASTE HEAT OUTLET FOR HOT ZONE AIR REGENERATOR.
SECTION "C-C-C-C"
SECTION "D-D"
SECTION A-A
FURNACE ZONE
SECTION B-B
SECTION "E-E" SAME AS "B-B" EXCEPTING GAS MAIN AND GAS CONNECTIONS ARE OMITTED
PREHEATING ZONE
GAS MAIN
GAS SHUT OFF COCK
GAS REGULATING COCK "G"
WASTE HEAT SHUT OFF VALVE
SUCTION REGULATING DAMPER
WASTE HEAT FLUE
AIR INLET VALVE
"F"
"F1"

FIG. 8.

View 1 shows a plan, from which it will be noted that the kiln is divided into 27 sections, not counting the ante and post chambers. Of these sections thirteen are included in the furnace zone and seven at each end in the preheating zones.

View 2 is a double cross-section. On the left hand side is shown the preheating zone; on the right hand side the furnace zone. It will be understood that in both of these zones the kiln is symmetrical about the center line.

View 3 is a side elevation of one section showing method of operating gas and air valves and the connections to the exhaust ducts.

View 4 is a sectional plan through one pair of regenerators and combustion chambers.

View 5 shows in more detail the method of controlling the air inlet to the air regenerator and the exhaust from the latter.

The kiln illustrated is designed to be burned with producer gas and in the furnace zone there are shown separate air and gas regenerators. Where other fuels are used the gas regenerator is not required and only a single air regenerator is used.

Assuming that the draft is on the flue (F′) the gas cock (C) is open, and the air valve (H) is open (see views 2, 3, and 5).

The gas and air pass through their respective regenerators and out into the ducts (J) and (K) which bring them independently into the chambers (L) whence they pass out among the loaded brick on the cars through the ports (M). In the highest heat zones the gas and air pass out separately into the kiln chamber and mix and burn there, so as to avoid destroying the refractories of the kiln. In lower temperature regions the gas and air pass into the same chamber and emerge mixed through the ports (M) into the kiln.

On the other side of the kiln the flue (F′) exercises a suction on the two regenerators through the connections both of which are controlled by dampers. The draft is communicated to the chambers (L′) and the gases entering the kiln chamber on the far side are drawn back through the ware across to ports (M′). These ports are adjusted initially to give the proper distribution of draft and fuel from top to bottom. But further changes in their size and distribution can be made while the kiln is in operation by inserting or removing, through the openings provided in the crown, small blocks fitting in the ports. Since the ports are the same on both sides of the kiln, the draft at any level will be proportioned to the fuel and air passing in to the kiln at the opposite side on the same level.

The gases pass through the regenerators, heat up the checkerbrick and then emerge into the waste heat flue (F′).

After a predetermined interval the gas and air are cut off, the draft reversed to flue (F) gas and air turned on again at the other side of the kiln. The process is then exactly the same but the gas stream passes in the opposite direction.

The mechanism by which these reversals are brought about simultaneously throughout the firing zone of this kiln is shown in view 3 and is one which has been used satisfactorily for years on by-product coke ovens.

On either side of the furnace zone the outgoing cars are heating up the incoming ones. In order to secure perfect heat distribution in this region a single regenerator chamber is provided on each side permitting a slight reversible draft to be maintained. A little gas is burned on the outside of the incoming car to insure its being heated evenly throughout. At the entrance end of the kiln chambers are provided in which the heat interchange between the two trains is carried out exclusively by the natural circulation of the atmosphere. It will be understood that relative proportions of these various zones can be varied to suit the circumstances.

In the case of the second type of kiln, where only one train of cars is used, the construction throughout the preheating zone is similar to that described save that the necessary amount of gas is burned on both sides of the kiln and some preheating can be done by displacing a proportion of the gases from the furnace section forward towards the entrance end. Only one set of regenerators, however, is provided in this region, the double regenerator system being confined to the furnace zone. In the cooling zone the same single regenerator construction is used but no fuel is burnt. The air passing in is preheated by contact with the checkers and strikes the brick on the cars at a temperature approximating their own. It passes out on the far side, heats the checkerbrick and escapes at relatively low temperature to the flue, which in this case is separate from the heating zone flue. In this way a very complete control of the rate of cooling in all sections can be obtained and where there is a need for large quantities of hot air for drying purposes this design is especially suitable.

The advantages of this cross-fired type of kiln can be summed up as follows:

(1) A kiln of great width can be built. It is felt that a width twice that of the ordinary longitudinal draft kiln is quite practicable. This enables the kiln length to be shortened and permits of large tonnages being fired in a single unit of practical length even when a very long cycle is necessary. The cross-section illustrated has 12 brick in the width. The pair of cars six feet long holds 3600 brick giving on 120 hour cycle a capacity of 42,000 per 24 hours for the 366-foot kiln.

(2) With regeneration of heat, the temperatures that can be reached readily are limited only by the failure point of the refractories of which the kiln is built.

(3) The kiln is, in essence, a series of independent short kilns, side by side. The conditions in each of these can be varied quite independently

of each other. In any section any desired atmospheric condition can be maintained, whether oxidizing or reducing, and in addition as much heating or cooling as is desired can be carried out.

Although the cross-fired regenerative type of kiln has principally been evolved to meet the condition of the silica brick industry, yet it is, of course, applicable to the firing of ordinary fire clay brick where very large tonnages, up to 200 tons per day, are required to be produced in a single unit or where only a short length is available.

Summary and Conclusions

For the heavy clay refractories the muffle type of kiln is best adapted owing to its inherent qualities of control and regularity of heat treatment.

For the fire clay fire brick the longitudinal draft direct fired kiln is indicated by its simplicity of design and cheapness of construction. The problems of firing this material do not seem to be beyond what can be successfully dealt with in this type of kiln.

For firing silica brick and other high fired refractories the cross fired regenerative kiln is best suited since it permits a practical volume of production on a long cycle, without extending the kiln to an inordinate length, and at the same time gives complete independent control of every stage of the heating up and cooling down.

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EUROPEAN SILICA REFRACTORIES

By Sandford S. Cole[1]

ABSTRACT

This investigation was on the silica brick and shapes made in Europe and the ganister supplied for the same. Analyses of rock and brick produced according to American practice and in Europe from the same rock are given. The results of tests on the best grades of brick are given. A general conclusion is that silica brick manufactured in Europe is not satisfactory for use in coke oven construction with a few exceptions.

Introduction

In an investigation on silica refractories manufactured in England and on the Continent, certain points of comparison have been found which might be of interest to the American manufacturers and users of silica refractories. In this work, a thorough study was made of the brick and shapes of the principal European producers of silica and of the main sources of supply of ganister in order to make a comparison with American rock and brick and to show the quality of the ware and the possibilities of its safe use in coke and gas oven construction.

Test of European Ganister

The ganisters were first investigated in order to see if a good grade of brick could be produced when the rock was handled according to American practice. The rock was worked in 1000-pound batches in an American silica plant under the same conditions of manufacture as American silica brick. The brick produced were tested for strength, fusion, apparent specific gravity and load test to 1500°C.

The ganister used had the following analyses:

	A	*B*	*C*	*D*	*E*
SiO_2	98.16	98.54	97.54	96.52	98.00
Al_2O_3	0.72	0.61	1.19	1.94	0.93
Fe_2O_3	.67	.51	0.21	1.42	.54
CaO	.36	.03	.35	0.07	.07
MgO	.01	.01	.01	.09	.07
Alkalis	.07	.07	.16	.06	Trace
Ignition loss	.30	.48	.42	0.37	.29

The results of some of the tests made are given below.

	B	*C*	*D*	*E*
Fusion cone	30–31	30–31	31–32	31–32
Apparent specific gravity	2.354	2.338	2.357	2.362
Modulus of rupture in lb. per sq. in.	730	774	483	529
Per cent permanent expansion after load test to 1500°C	0.98	1.05	1.09	1.21

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[1] Industrial Fellow, The Koppers Company, Mellon Institute, Pittsburgh, Pa.

The sample marked *E* made an exceptionally fine brick which on reheating to 1500°C became very nearly clear white in color. All the brick made gave a sharp ring when struck with a hammer. Only with *D* was there any difficulty encountered in production, it being inclined to stick to the molds and was rather plastic.

The following are the analyses of the brick. *D* and *E* were made using 10% "bats" from a batch in which no "bats" had been used.

	B	*C*	*D*	*E*
SiO_2	95.90	96.34	94.04	95.94
Al_2O_3	1.09	0.75	1.73	0.73
Fe_2O_3	0.80	.87	1.11	.79
CaO	1.89	1.93	2.92	2.45
MgO	0.06	0.21	0.14	0.11
Alkalis	....	....	.17	.11
Ignition loss	....	0.03	.02	.06
	99.74	100.13	100.13	100.19

Conclusions It is possible to produce as good brick for coke and gas oven construction from these as can be produced in this country. The ganisters were very similar in appearance and structure to the Medina sandstone strata used in the production of a large portion of the silica brick in this country. The silica brick and especially that made from *E* was quite promising and gave evidence of a good grade of rock being at hand for use.

Foreign Made Brick

The brick and shapes manufactured in Europe were then investigated and in general the ware was of a fair workmanship and quality but the brick were not well bonded, were underfired and low in fusion point. In the investigation of ten manufacturers of silica brick there was found to be but two whose products were comparable with the American grades. The general cause of failure to meet with requirements was low fusion, high specific gravity and failure under load of 25 lb. per sq. in. The high specific gravity is an evidence that they either have difficulty in firing, or their kilns are not of proper construction to reach the temperature required to give a partial or complete inversion of the quartz to cristobalite and tridymite. The general value for the specific gravity was from 2.40 to 2.45 with a fusion point ranging from 29 to 31. A further proof of the low firing was in the permanent expansion in load test.

To see if this expansion was due entirely to underfiring, a reheat in kilns in this country was made and an expansion of nearly the same value as on load test was obtained. When these brick were subjected to load test and a low permanent expansion resulted, it proved that the brick had not been fired to a sufficiently high temperature.

The results on the satisfactory brick are partially given below.

	A	*B*
Fusion point	31–32	32
Apparent specific gravity	2.38	2.329
Permanent expansion on load test to 1500°C	1.73%	0.36%
Permanent expansion on load test to 1500°C (after reheat in commercial kilns)	0.55	..
Modulus of rupture	537	377

CHEMICAL ANALYSIS

SiO_2	94.36	96.52	MgO	0.11	0.07
Al_2O_3	2.16	0.51	Alkalis	.28	.17
Fe_2O_3	0.69	0.49	Ignition loss	.49	.04
CaO	1.68	2.02			

These two sets of brick were quite similar in color and in other properties to American made brick. The brick was produced from *B* ganister and had an exceptionally smooth surface and sharp lines due to the molds used by the manufacturers. The results on these brick give a concordant value with those usually had on American made brick. The analysis is quite similar with the average of the Eastern silica brick. The one low modulus of rupture has probably been caused by a weakening of the brick by rough handling in transportation.

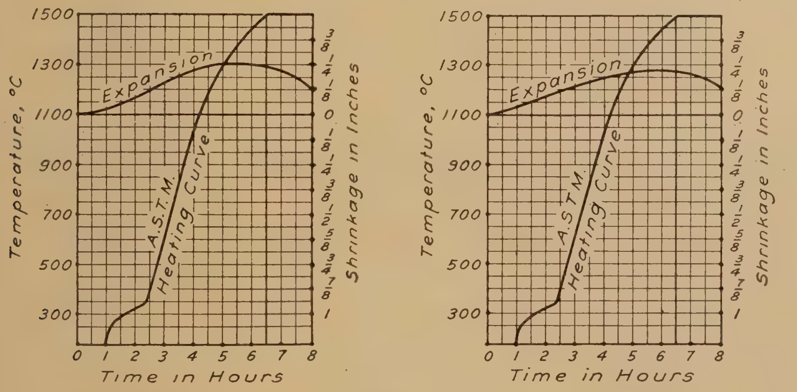

FIG. 1.

The general conclusion drawn from this investigation is that the European silica users have a lower standard than the American. There was found to be a general tendency toward Dinas and quartzite brick quality and class. Some of the brick and shapes gave quite conclusive evidence that they were bonded with clay. Then, too, the ganister used may have some effect as there are quarries which do not produce as good a grade of rock as those which were tested.

Silica Cement

Two silica cements were also tested. The results of the screen test, fusion, and change in firing to cone 15 and 20 are given here.

Screen test	*A*	*B*
On 20-mesh	....	....
48	1.67%	17.4%
100	8.80%	20.0%
200	8.85%	13.3%
Through 200	80.68%	49.3%
	100.00%	100.0%
Fusion cone	19	31
Drying shrinkage		1.3%
Firing shrinkage, cone 15	....	0.0%
cone 20	....	+1.8%

Both were quite plastic but the fineness of grind of *A* caused the low fusion point. *B* was quite similar to the American cement in both screen analysis and appearance.

Screen analysis (100 samples avg.) of American made silica cement shows:

Mesh	Per cent	Mesh	Per cent
On 20	..	On 200	12.0
On 48	20.0	Through 200	38.0
On 100	30.0		

Although *B* was rather fine it met the fusion requirements, and the slight expansion from wet to fired length at cone 20 makes it entirely possible to be used to set up silica in coke ovens.

SOME DATA ON THE PULSICHROMETER[1]

By Robert Galbraith

ABSTRACT

A table has been worked out of the plate openings necessary to use with enamel and slips of different weights reducing the skill required to obtain a smooth coating on a piece. The apparatus is described and tests were run on varying materials, *viz.*, raw materials, fritted enamels and slips. The theory is advanced that the large orifice fails to develop enough back pressure to give the enamel sufficient velocity through the tube. Other features of the pulsichrometer are discussed.

It is recognized by operators of the pulsichrometer that when a slip of relatively low specific gravity is used with an enamel of a higher specific gravity, the slip will precede the enamel when going up a perpendicular piece, whereas the slip will follow the enamel when the direction is reversed. On the suggestion of M. E. Gates a table has been worked out of the orifices or plate openings necessary to use with enamels and slips of different weights in order that "following" may be eliminated. This reduces the skill and care required to obtain a smooth, even coating on a piece.

Table I shows the diameters in inches of the standard plates used.

No. of Drill	Inch Diam.
70	0.028
65	.035
60	.040
57	.043

There is a difference of 0.015 inch between the largest and smallest drill hole. This will be shown to have a weighty influence upon the action of the machine.

The set up of the apparatus to work out these orifice relations is shown in Fig. 1. The machine was fastened rigidly to one end of a shaft by set screws. The shaft was then fitted to a collar which held it securely. At the opposite end of the shaft a circular disk was mounted which was free to revolve about the shaft. This disk was made to revolve at a fairly uniform speed of 216 r.p.m. The machine was operated at a constant speed of 800 r.p.m. as that is the average speed used by the machines in the slipping department.

Sheets of unexposed blue print paper were cut round to fit the disk. The disk was set in motion and the enamel sprayed upon it. Every spot of enamel left a white mark on the paper, which of course turned blue after exposure to light, and in this way a permanent record was obtained.

The average distance from the center of the spots to the center of the chart was then measured and the specific gravity and flow of the material

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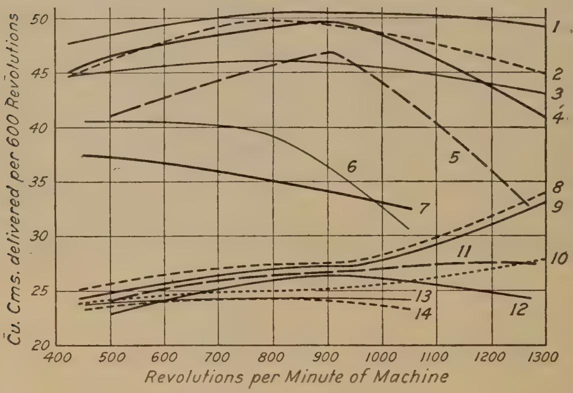
[1] Presented at the Atlantic City Meeting, February, 1924 (Terra Cotta Division). Received September 24, 1924.

noted. The specific gravity was obtained by weighing 100 cc. of the material. The flow was measured by means of a flowmeter. This flowmeter was a cylinder of $2^1/_8$ inches diameter and 7 inches length at one end of which was a cylindrical tube of $^3/_{16}$ inch diameter and 6 inches length. At the other end of the cylinder there was a hole of $^3/_8$ inch diameter.

A wide variety of materials was used, the list consisting of three fritted enamels, two raw enamels, a fritted glaze, and three slips. After running materials of certain viscosity and specific gravity they were thickened with acetic acid which gave slower flow with but a slight change in specific gravity. The material was then thinned down with water to the same flow it had before the addition of acid. A series of four standard plates was used for each setting of the material.



Curve	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Plate	None	57	70	57	70	57	70	None	57	70	57	70	57	70
Hose	4	4	4	4	4	4	4	3	3	3	3	3	3	3
Flow				45	45	71	71				45	45	71	71
Material	Water			Slip		Enamel		Water			Slip		Enamel	

FIG. 1.

After making a number of these charts it was realized that the speed of the machine was probably as large a factor as anything else in determining the height at which the material would strike a piece. Consequently some delivery data was obtained. The machine was set at different speeds, noted by the use of a stop watch and a speed counter applied to the end of the shaft which operated the pedals. After obtaining the speed, the material delivered for a certain number of revolutions was obtained by catching it in a test tube and weighing it, measuring the specific gravity of the material and dividing it into the weight delivered, calculating the cubic centimeters. Curves were plotted using the revolutions per minute of the machine as abscissas and the cubic centimeters delivered as ordinates. Upon comparison of these curves with the ones obtained with the machine running at constant speed, it was decided to concentrate most of our attention on the latter experiments as these seemed to show more clearly just what does occur in the pulsichrometer.

As a consequence of this decision this chart has been prepared (Fig. 1). You will observe that three materials have been used, water, slip, and enamel. Two hose have been used with the respective diameters $^3/_{32}$

and $^1/_8$ inch for number 3 and number 4. The areas of the hose calculated in square centimeters are .0445 and .0792. The orifices used were numbers 57 and 70, .043 and .028 inch in diameter.

There are several interesting facts shown by these curves and I have endeavored to derive a theory for most of the more unusual features. The intersections of the curves show the speed at which to run the machine in order to have the same quantity of material delivered using the plates and hose indicated. These points were all checked by actual experiment. The highest points of the curves should be the ideal speed at which to operate the machine in order to gain a maximum output, enabling the operator to finish a piece more quickly. These points were also checked. One interesting point on the chart is the intersection of the curves for the enamel using a number 4 hose with plates number 57 and 70. My own tentative theory to account for this is that the larger orifice fails to develop enough back pressure to give the enamel sufficient velocity through the tube.

Another interesting feature is the close proximity of the points for the different plates when a No. 3 tube is used. This must be due to the diameter of the hose being so nearly the same as the diameter of the orifice. The fact that at high speeds all the curves (except those using water in No. 3 hose) decrease in height must be due to the rapidity with which the pedal strikes the tube, not allowing a sufficient interval of time to elapse for the hose to fill up before an expulsive action occurs.

The convexity of the curves for water using a No. 3 hose apparently indicates the water has sufficient velocity in the tube to allow it to completely fill between impacts, thus causing the amount delivered to vary directly with the speed. It is regrettable that the machine could not be operated at a sufficiently high speed to determine the maximum for this curve.

Discussion

MR CLARE:—Did you make these experiments because you were getting variations?

MR. GALBRAITH:—We wanted to see if we could not stop this shooting up of the slip. I started out to get up a table using two different materials with varying specific gravity and viscosity of flow to see if we could arrange a series of plates so they would all hit the same, so that a piece could be worked up or down or sideways without variation.

MR. CLARE:—Would that variation change the character of the texture you were making?

MR. GALBRAITH:—Very much. If one man should get a sudden notion to go down on a piece while the other man was going up, one piece would be very dark while the other piece would be light. You would have great variation.

MEMBER:—What is the density you use on vases?

MR. GALBRAITH:—1.75 grams per cc. and for raw enamels we usually set around 1.7 grams per cc.

MR. RADCLIFFE:—I have used it in various ways and with a slip in the middle. The slip did run ahead. When we first got the machine we were instructed to use it any old way and that it would work, but we found that in order to produce a uniform color we had to go the same way all the time. If a sprayer started at the bottom of a piece and went to the top he would get just about the same color. However, if he shot at an angle he got long streaks, whereas if he held the machine so it shot directly at a piece he obtained more uniformly shaped spots.

We have used it mostly with a slip in the center hose and a glaze in the outside hose. I think if you use two glazes or two slips you have less trouble from variation of color than you do by using a glaze and a slip.

It gives good results providing you keep it in good shape. The pulsichrometer, in order to work properly, must be gone over practically every day and cleaned and oiled up. If your spots vary it is for the simple reason that the glaze does not flow through your hose fast enough to fill it up before these plates come up and squeeze the hose. The hose does not have time to fill up if your machine is running too fast and you may get more of the slip spots than you want. If it runs at a fair speed it does very well.

MR. SCHEPERS:—I have personally run a machine for six months using it day in and out, for three or four hours at a time. The machine has never been taken down and I never took the plates off or have never had any trouble with it. When I got through with it, I shot some water through and laid it over on the side. I have never had any experience where the machine should be oiled or cleaned every day.

MR. STRUSHOLM:—We have four of those machines working at the South Amboy Terra Cotta Company and if the man using a machine does not clean it, it delays us some minutes before we can get it to working. If you leave the pressure on, the small hole closes up entirely and there is only one remedy and that is to cut a piece off. You never saw a piece of machinery from an automobile to a threshing machine that did not want cleaning and care and oiling.

MR. HOTTINGER:—It seems to be but a precaution to always put a machine away in such shape that it can be used the next day and also to take care of it.

MR. STRUSHOLM:—We were told that these machines would break down every day. We have used them for a year and the only breakdown we had was because one of the men let a machine fall and did not report it.

SYNTHETIC SILLIMANITE IN CERAMIC BODIES[1]

By T. S. Curtis[2]

ABSTRACT

The manufacture, characteristics, and use of a new ceramic product in which the stable form of sillimanite, having a composition of $3Al_2O_3$–$2SiO_2$, is the chief constituent. An interesting feature of the product is the fusible matrix of definite composition, in which sillimanite needles are held, and which permits of recrystallization at commercial temperatures when the product is added to porcelain or whiteware body mixes. Introduction of sillimanite apparently greatly toughens and strengthens the body in which it is introduced.

Introduction

When the Research Division of the Vitrefrax Company started an investigation of the properties and possibilities of sillimanite, the literature was meager and of doubtful practical value. Since that time, much work has been done with this remarkable compound, and during the past year a number of valuable papers have appeared on the subject, chiefly, if not wholly in the *Journal of the American Ceramic Society*. It is proper to make acknowledgment to those able and zealous workers of the Bureau of Mines at the Northwest Experiment Station for their practical help in this field, also to the investigators of the Geophysical Laboratory.

Early Investigations

Our experimental work has covered what we believe to be every known form of sillimanite. Andalusite, cyanite, and natural (Indian) sillimanite have been used, as well as every conceivable artificial mixture, from chemically pure aluminum oxide and pure crystal silica, to the diaspores and bauxites.

In every case, we have found heat treatment to change the mineral or the mixture into a mass of crystals having a composition of 71.8 alumina to 28.2 silica. This represents a molecular ratio of $3Al_2O_3$–$2SiO_2$. This fact was determined first by carefully removing the needle-like crystals from our first ingots with tweezers and analyzing them chemically. In the heart of every ingot having approximately a 1:1 ratio as charged, there will be abundant masses of these crystals.

We then found that near the matrix from which the needles grew apparently a sheath of glass covered the crystals, changing their apparent composition to one between 3:2 and 1:1. Small bundles of crystals were then placed in cold hydrofluoric acid for several hours to dissolve the glassy sheath. The cleansed crystals then showed a ratio of exactly 3:2 on chemical analysis.

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[1] Presented at the Summer Meeting, Los Angeles, Calif., October 6, 1924.

[2] Director of Research, The Vitrefrax Company, Los Angeles, Calif.

We followed by sintering at cone 36 an intimately ground mixture of alumina and silica in the ratio of 1:1, after which the ground sinter was leached with hydrofluoric acid as before. The washed residue analyzed 3:2 in ratio.

Our slowly dawning conclusion that the stable compound of alumina and silica was something other than what we had learned from the published curves was confirmed very quickly when refractory brick were made from the various melts. The 3:2 brick were strong and rigid under loads at high temperature, while those having a composition of 1:1 were not able to bear loads as well as a good fire brick, although the melting point of cones made of the two melts was about the same.

Ceramic and Refractory Sillimanite

The results of this early work quickly showed that there might be two entirely distinct and valuable uses for sillimanite. One, as a refractory, in which the ratio of the entire product would have to be 3:2 while the other, a development of sillimanite 3:2 crystals in a matrix of rather definite composition, might have important applications as a ceramic material.

The refractory grade was found to be entirely too refractory to be satisfactory as an ingredient in ceramic bodies, since it consists chiefly of 3:2 crystals and corundum plates. By firing a porcelain body at excessively high temperatures, probably the same results could be obtained as with the ceramic grade of material. But this was considered to be impracticable. Our problem was therefore to so combine as to permit the formation of an easily fusible glass of definite and controllable composition in which an abundance of 3:2 sillimanite crystals would grow as the melt cooled. The theory was that in such a product, when combined with a typical ceramic body mix, the glass would readily melt into the body, forming an addition having the same function as feldspar, and permitting the sillimanite crystals to grow anew and to interlock in a tangled mass within the body.

The problem was simple insofar as making a fusible glass was concerned; practically any ratio from that of kaolin to near that of 3:2 sillimanite would give it. But in nearly all of these mixes great difficulty was experienced in removing microscopic pellets of metallic impurities which spotted the ware made from the product.

Finally, however, a composition was evolved which gave precisely the characteristics desired, and it was found that by a very careful control of the raw mix and of the subsequent furnace operation, a remarkably consistent and uniform product resulted.

It is an interesting commentary on the mysteries with which the compound called sillimanite surrounds itself to note that chemical analysis of the finished product does not in any way suggest how to duplicate it, for the composition of the raw mix bears very little resemblance to the melted and crystallized material coming from the furnace. It was this feature of the work that caused the investigators seemingly endless effort before a controllable product materialized.

After the final product was evolved, it was found that due to the reducing atmosphere under which it formed, slight traces of free alkali would persist after crushing and grinding. This alkali would act as a deflocculant in many bodies to which the grain was added, serving in some cases utterly to destroy the plasticity of the body. A treatment has been developed to eliminate this troublesome feature entirely so that the addition of the finely ground product has no more effect than so much feldspar or flint on the working properties of the body.

The removal of entrained metallic impurities offers perplexing problems. We very quickly discovered that the addition of metallic iron to the charge to render the particles of reduced silicon magnetic would ruin the color of the final product, for, contrary to the prevailing opinion, we found that sillimanite would take up and hold in solid solution sufficient iron to turn the crystals deep amber color when they are oxidized.

We have found that by a decidedly limited raw mix composition and certain method of furnace operation in which the power input per pound of charge fed into the furnace is controlled within close limits, we can make even the microscopic shot of silicon magnetic so that they may be removed by powerful, high intensity magnetic concentrators after the product is ground.

How Product is Used

In order that the peculiar value and effects of this product may be understood, we shall use as illustrations some familiar applications of the principle of fibrous aggregates that may cause some of our learned members to smile; the principle is so beautiful in its simplicity and strength, however, that we must make certain that it will be understood, even by those to whom sillimanite is quite unknown.

If you will let your minds slip back to the historic days when unbaked brick were made with straw; if you will recall that the plasterer admixes hair with his plaster, and those of you who make terra cotta will surely picture how frail a plaster mold without its fibrous aggregate would be; if you will think of the value of asbestos fiber in many cold and hot cements; and finally of the strength which is imparted to common concrete by the interlacing network of steel fiber within it; and then think of the cement which binds concrete as a mass of millions of tiny interlacing crystals so entangled as to impart not only great rigidity but toughness to the bonded mass of aggregate, then you will in a measure visualize the function of sillimanite in a ceramic body.

As any mixture of alumina and silica with fluxes is brought up to a temperature where the mass, or at any rate that part of the mass in contact with the impurities, becomes viscous or fluid, a small percentage of the body will become liquid. As this liquid cools, tiny needle-like crystals of sillimanite will grow in the congealing fluid, just as salt crystals grow out of a cooling and evaporating solution of salt in water. We have every reason to believe that much of the strength and toughness of porcelains is due to this interlocking network of sillimanite fiber which develops in the body on cooling.

But in the common porcelains, a very small amount of sillimanite is formed for the reason that the firing temperatures employed do not take more than the matrix surrounding the crystals of kaolin and of flint into solution. We have found that on melting ordinary fire clay, an abundance of sillimanite crystals appear in the melt after it has cooled. Therefore it is reasonable to expect that if it were possible to fire an average porcelain sufficiently high, a very much larger percentage of sillimanite would form in it. However, that treatment would hopelessly ruin the ware, since there would not be nearly sufficient sillimanite-forming ingredients in the body to cause it to retain its shape in the firing.

The answer must be apparent. In order to produce a piece of ware in which great strength and toughness are indicated, we must build the foundation or skeleton of that body of a mass of strong, tough fibers having a very low coefficient of expansion, preferably building up such a percentage of the needle-like crystals that the latter will interlace and interlock. Then we must fill the interstices of this fibrous mass with a bond in which still more fibers will grow in ever decreasing size as the voids decrease.

The new ceramic product we have described has just this for its function. Rich in pure sillimanite crystals, yet imprisoned in a matrix which permits a ready blending and solution with the ball clay and china clay of the bond at temperatures within commercial reach, acting in itself as feldspar in the high fire bodies, and combining readily with the feldspar in those compositions designed for lower firing temperatures, the product offers extremely interesting and important fields of investigation by makers of porcelain and whiteware bodies.

The electrical properties of the product are excellent and its use in many forms of electrical insulators seems assured once its properties are understood.

While no work has been done with the product in the manufacture of glazes, it appears to offer possibilities if one may judge by its behavior in refractory cements designed to glaze or flow at furnace temperatures. When admixed with ball clay and feldspar and applied as a wash to fire brick, a fine, tough glaze is formed at slightly above cone 20. This glaze appears to resist mechanical injury very well after cooling and shows no tendency to craze when applied either to siliceous or aluminous clay brick. It is to be expected that an element of toughness would be introduced in glazes through its use.

In itself, sillimanite appears to have practically no covering power as an opacifier, although it has been used as such in opal glass, so we are informed. The crystals are clear and colorless, while the streak is white.

It would therefore appear as though the product could be used in either transparent or opaque glazes, although in the former the tendency to crystallize in a myriad of satin-like needles may mitigate against its use. We have observed in the refractory glaze previously referred to, only a slight tendency to show this satin appearance to the naked eye, while under the microscope, the apparently transparent glaze is really a mass of fine, hairline needles, apparently distributed in the utmost confusion.

The use of synthetic sillimanite of the ceramic type in balls for pebble mills as well as in the linings has been shown to have a truly practical value. In the fine grinding of the product, we use Durox balls exclusively. We have used pieces of the furnace ingot, which form in pebbles in the large mills at times, for months of continuous grinding with practically no measurable wear. If it were commercially possible to produce these pebbles in quantities at a reasonable cost, the flint pebble would be driven from the market, as the sillimanite pebble has a specific gravity of 3.1 against about 2.6 for the flint, and its wearing qualities are amazing.

While the bonded sillimanite does not have quite the wearing qualities, nor has it the specific gravity of the original ingot ball, it nevertheless shows such an increase in grinding efficiency that its use to the exclusion of flint pebbles seems fully justified.

The introduction of this new form of sillimanite product does not adversely affect the color of a white body when the addition is made of the specially treated ceramic grade of material. The burning color is pure white.

Ceramic Sillimanite Made Commercially

The product we have described is well out of the experimental stage insofar as its manufacture is concerned. It is produced in a plant having a daily capacity of 20,000 pounds of which capacity approximately one half is now utilized. The raw material resources guarantee uninterrupted production entirely independent of any foreign material. The uniformity of the material is remarkable, due to the close control necessarily exercised in its manufacture.

The use of the product is, however, entirely in the experimental stage, with the exception of two commercial applications which have proven so successful that a steadily increasing tonnage is being manufactured.

The results that may reasonably be expected from the introduction of sillimanite into many ceramic bodies are of such moment that it would seem to justify considerable investigation on the part of whiteware makers, porcelain insulator manufacturers, and other ceramic workers who desire to impart considerably greater strength and toughness to their wares. To this end, the manufacturer of the specially prepared ceramic grade of sillimanite which has been described in this paper, will be glad to furnish samples for experimental purposes to any manufacturer who is interested.

METHOD FOR THE ANALYSIS OF ALUMINOUS SILICATE REFRACTORIES[1]

By Edward P. Barrett[2] and Frederick W. Schroeder[3]

ABSTRACT

A method is given in which the solution of difficultly fusible refractory material is obtained by subjecting the finely pulverized material to two fusions, the first in sodium carbonate, followed by one in potassium bisulphate. The melts are dissolved in water and after adding sulphuric acid are evaporated to dense fumes. Care is taken to remove any calcium sulphate that may be formed. The final residue is treated with hydrofluoric and sulphuric acids. The alumina is determined according to the method described by Blum as given by Hillebrand especial care being used in heating the final precipitate to constant weight. A temperature of about 1150°C is necessary. Two precipitations are required in the determination of lime. The excess of ammonium salts are removed prior to the precipitation of the magnesia, by adding an excess of nitric acid, evaporating to dryness and heating, which expels the ammonium chloride according to the reaction $NH_4Cl + HNO_3 = HCl + 2H_2O + N_2O$.

Introduction

The analysis of fused clays and artificial sillimanite is a difficult problem due to the infusibility of these substances with any of the common fluxes. Samples of fused clay and artificial sillimanite, ground to pass 300-mesh, were mixed with ten to thirty parts of sodium carbonate in a platinum crucible and heated over a blast lamp for as long as five to six hours. These melts were cooled and taken up with hot dilute hydrochloric acid. In every case there remained a residue of unfused material. In a number of cases this residue was pulverized in an agate mortar, mixed with sodium carbonate in a platinum crucible, and heated over a blast lamp for over an hour. Upon cooling and taking up with hydrochloric acid there appeared to be as much residue as before the second fusion. Attempts to obtain fusions with potassium carbonate, with mixtures of sodium and potassium carbonates, and with potassium bisulphate were equally unsuccessful. A two-fusion method was suggested in which the material was fused in a platinum crucible with potassium bisulphate, the melt cooled, taken up with hydrochloric acid, filtered, and the residue ignited and fused with sodium carbonate. A few trials showed that an unfused residue remained after the second fusion.

The pulverized fused clays and artificial sillimanites are easily fusible in sodium peroxide in iron, nickel, or silver crucibles but alumina cannot be determined in solutions obtained from fusions in sodium peroxide in iron or nickel crucibles because of the large amounts of iron or nickel taken into solution. It is difficult to remove silver from the silica in solutions obtained from the fusions in silver crucibles. Then, too, any silver remaining in the silica might alloy with the platinum crucible during the ignition of the silica and alumina precipitates. The life of the silver crucibles is short, about ten fusions being all that can be obtained from each crucible. A satisfactory method using peroxide fusions in silver crucibles was perfected. Its use was discontinued because of the large number of manipulations required.

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[1] Published by permission of Director U. S. Bureau of Mines.

[2,3] Assistant Metallurgist and Junior Chemist, respectively, Northwest Expt. Sta. (Seattle, Wash.) of the Bur. of Mines. In coöperation with College of Mines, Univ. of Wash.

Fusions in mixtures of borax and sodium carbonate were suggested. Borax glass was prepared by fusing C.P. borax in a platinum crucible and pouring the melt onto a polished iron plate. Two or three grams of this borax glass added to ten to thirty parts sodium carbonate are sufficient to give perfect fusions in about thirty minutes heating over a Meeker burner. The only objection to this method is that it is very difficult to remove all of the borax, which contaminates both the silica and the alumina.

A satisfactory method was finally worked out in which the refractory material is subjected to two fusions, the first in sodium carbonate, followed by one in potassium bisulphate. The complete methods for the analysis of refractory ceramic materials follows.

Procedure

Fusion Mix 0.5 gram of the refractory material, ground to pass 200-mesh with about five grams of sodium carbonate in a platinum crucible and heat for twenty to thirty minutes over a Meeker burner. Take up in water and dilute sulphuric acid. Filter, ignite and fuse in several grams of potassium bisulphate. If considerable gelatinous silica is left after the sodium carbonate fusion, it is well to fuse in more of this flux before using the potassium bisulphate for the silica is liable to form a protective coating on the unfused material. The leachings from these various fusions are combined and about 10 cc. sulphuric acid added to the whole.

Silica Evaporate on the hot plate until copious fumes of sulphur trioxide are evolved. After cooling add about 200 cc. of water and boil for several minutes to insure the complete solution of calcium sulphate. Filter off the residual silica and wash well with hot water. Repeat this dehydration to remove the silica completely. Ignite the silica residues in an untared platinum crucible and weigh. Treat the residue with several cc. of hydrofluoric acid and one or two drops of sulphuric acid; evaporate and ignite. The silica is completely volatilized as silicon tetra fluoride, leaving the impurities in the form of the non-volatile oxides of alumina, iron, titanium, etc. The loss in the weight of the crucible and contents represents the actual weight of the silica.

Fuse the non-volatile residue in a small quantity of potassium bisulphate and add to the filtrate from the dehydrations.

Alumina and Iron[1] To the combined filtrates from the silica determination, made up to 400 cc., add approximately 10 grams of ammonium chloride, heat to boiling and add ammonia slowly until just alkaline to methyl red. Boil for a few minutes and then filter hot. Wash the residue several times with a 2% solution of ammonium chloride.

Evaporate the filtrate (No. 1) to a small bulk on hot plate. Digest the precipitate in 1:1 hydrochloric acid and reprecipitate exactly as before. Evaporate the filtrate (No. 2) from this precipitation to dryness and heat to expel ammonium salts. Take up the residue with hydrochloric acid and add it to filtrate No. 1. Add a little ammonia and continue evaporation to coagulate the last traces of iron and aluminum hydroxides. Filter and wash this small precipitate with a 2% ammonium chloride solution and add it to the main one.

Ignite to constant weight in a tared platinum crucible the combined precipitates of iron and aluminum hydroxides in an electric muffle furnace at 1150°C.

Determine the iron and other constituents by any of the well-known methods.

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[1] The method used for this determination is essentially that of Blum, as given by Hillebrand. W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," U. S. Geol. Surv., *Bull.* **700** (1919).

ENAMELING DEFECTS DUE TO THE CAST IRON[1]

By A. Malinovszky

ABSTRACT

Troubles in manufacturing sanitary enameled ware are pinholing, breaking out, blistering, crazing, chipping, lifting, black specks, etc., due to the iron, the chemicals, methods of applying the slush or enamel, furnace temperatures, inexperience, lack of cleanliness, differences of the coefficients between iron and enamel and fitting of ground coat to the enamel, etc. Feldspar is most liable to cause trouble by variations of its constituents. Feldspar containing above 69% of silica should be looked upon with suspicion. Troubles arising from the cast iron are discussed. Results of chemical analyses and microscopic examinations and microphotos before and after enameling are shown.

Chips and lifts are caused by globules and patches in the castings due to some of the metals passing through the cupola unmixed. Segregations of the graphitic carbon even in minute state produce blistering especially if the graphitic carbon is present in laminar form.

Blisters, if caused by the iron, seem to be governed by the condition and size of the graphitic carbon. The presence of slag or dirt in the castings or at the surface of the casting also can cause chipping, lifting, black specks and blisters.

A certain southern pig iron has produced segregations of laminar graphitic carbons which constantly gave blistering, chipping and lifting. No mixture of irons with this southern iron would be free from these defects. Microscopic examinations of blistered ware revealed black spots (patches) on the castings where the blistering occurred.

Samples of blistered ware were prepared for microscopic examinations and also for chemical analyses before and after the ware had been enameled in order to compare the two samples and to determine what had taken place in the iron. The samples which showed laminar graphitic carbons before enameling showed black spots after enameling where blistering had occurred.

Chemical Analysis In order to show the changes taken place during heating of the castings, three tubs were selected, one 5 foot roll rim, one 5 foot flat rim and one $5^1/_2$ foot flat rim. Drillings for the chemical analyses were taken from the rim, side and bottom. After enameling the drillings were taken $^1/_8$ inch from the place where the first drillings were taken. The results are the following:

Analyses of Cast Iron before Enameling

5 ft Roll Rim Tub:	T.C.	G.C.	C.C.	Si	Mn	P	S
Rim:	3.408	2.454	0.954	2.572	0.502	0.729	0.0685
Side:	3.545	2.727	0.818	2.544	0.506	0.728	0.0672
Bottom:	3.545	2.863	0.682	2.509	0.513	0.731	0.0679

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[1] Presented at the Summer Meeting, Los Angeles, Calif., Oct. 6, 1924.

5 ft. Flat Rim Tub:							
Rim:	3.436	2.672	0.754	2.486	0.487	0.731	0.0752
Side:	3.408	2.590	0.818	2.563	0.491	0.735	0.0748
Bottom:	3.545	2.808	0.737	2.544	0.492	0.733	0.0760
$5^1/_2$ ft. Flat Rim Tub:							
Rim:	3.572	2.372	1.200	2.516	0.476	0.734	0.070
Side:	3.517	2.372	1.145	2.52	0.478	0.735	0.0692
Bottom:	3.545	2.427	1.218	2.48	0.487	0.738	0.0688

ANALYSES OF THE CAST IRON AFTER ENAMELING

5 ft. Roll Rim Tub:							
Rim:	3.599	3.081	0.518	2.499	0.502	0.711	0.0683
Side:	3.517	3.136	0.371	2.507	0.506	0.713	0.0679
Bottom:	3.626	3.054	0.572	2.53	0.513	0.72	0.070
5 ft. Flat Rim Tub;							
Rim:	3.545	3.108	0.437	2.48	0.465	0.731	0.0713
Side:	3.408	3.381	0.027	2.499	0.468	0.734	0.0739
Bottom:	3.463	3.245	0.218	2.544	0.468	0.733	0.0726
$5^1/_2$ ft. Flat Rim Tub:							
Rim:	3.517	2.563	0.954	2.51	0.472	0.706	0.0692
Side:	3.599	3.217	0.382	2.479	0.472	0.706	0.0696
Bottom:	3.490	3.190	0.200	2.488	0.480	0.709	0.0670

One tank lid had been drilled on both ends before enameling. Analyses of the two end drillings gave the following results: Only the carbons had been determined.

	T.C. Before	After	G.C. Before	After	C.C. Before	After
End 1.......	3.408	3.545	2.699	3.217	0.709	0.318
End 2.......	3.408	3.545	2.699	3.217	0.709	0.328

This lid caused no blistering.

Microphotographs Fig. 1. The sample was taken from a blistered and chipped tub. Carbon occurs abundantly as graphite in large curved crystals. These are shown clearly in the photograph. The bulk of the sample is pearlite, free cementite occurs in minute needles and narrow bands separating the patches of pearlite or cutting through them. Some of the cementite shows a honeycomb eutectic growth.

Fig. 2. Cross-section of the same tub as Fig. 1. Graphite crystals mostly their flat side parallel this face. Some show the curved lines but these are not so abundant as in Fig. 1. The form and relation of the pearlite and cementite is the same on this face as on Fig. 1 except for direction of the graphite crystals. There is no difference between the two faces of these samples.

Fig. 3. This shows graphite in small curved flakes which intersects the face at all angles. They are smaller than in Fig. 1. Free cementite is slightly less than in Fig. 1, and the texture is coarser. The cementite

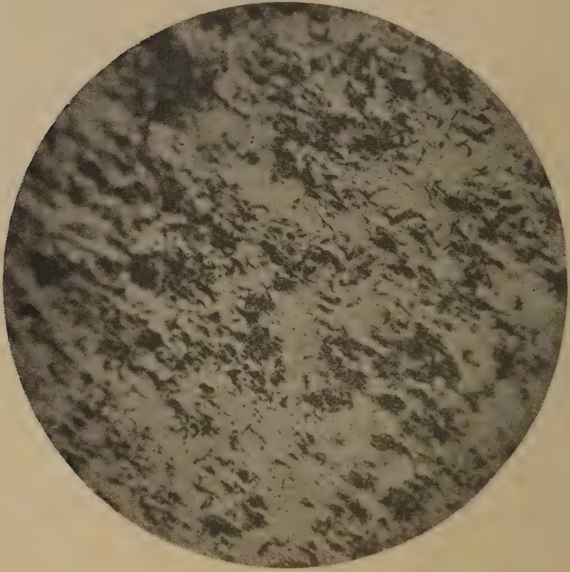

FIG. 1.—Unetched, showing graphite crystals.

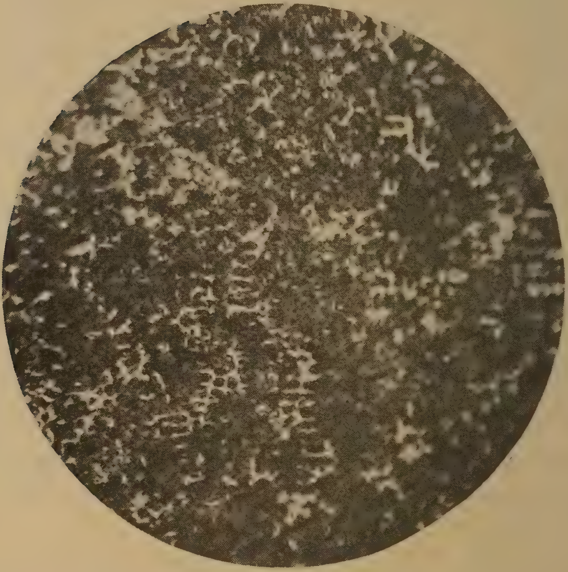

FIG. 2.—Etched, shows cementite (white) with honeycomb structure, pearlite (grey).

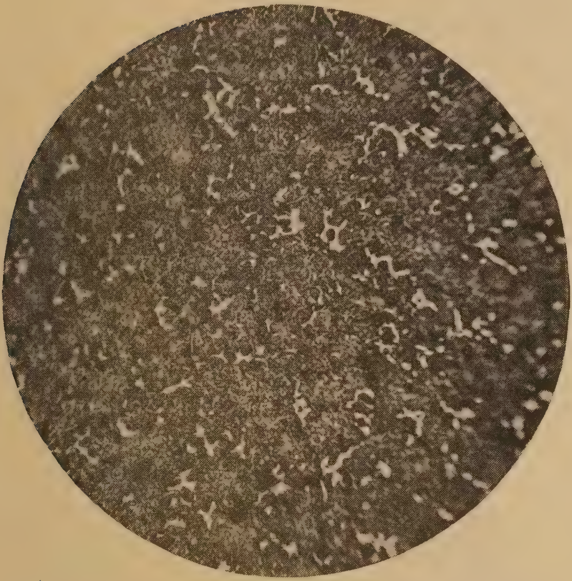

FIG. 3.—Etched, cementite (white), pearlite (grey).

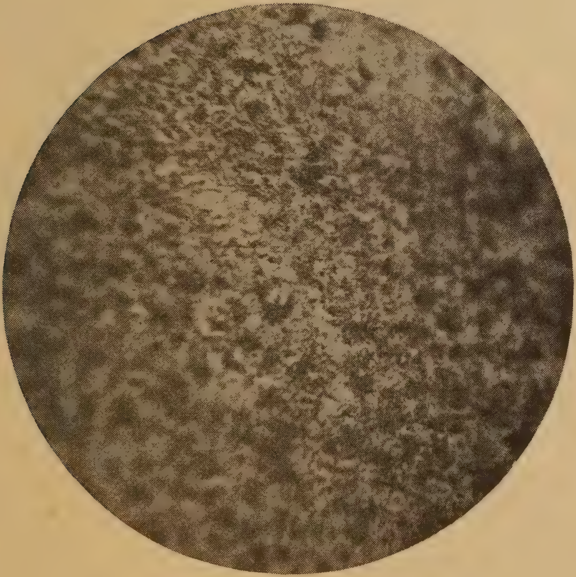

FIG. 4.—Unetched, shows graphite.

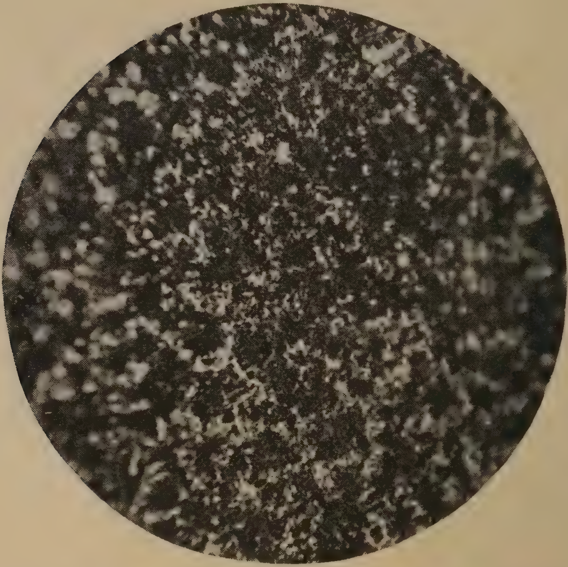

FIG. 5.—Etched, cementite needles (white), pearlite (grey).

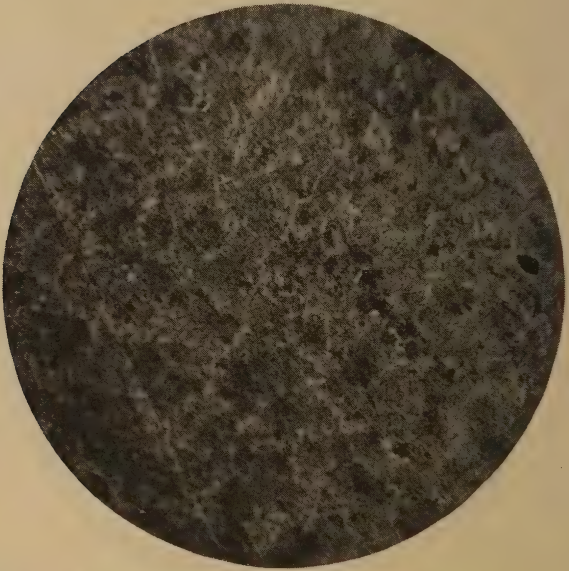

FIG. 6.—Faintly etched, shows mottling appearance, blotches of temper carbon.

not being so evenly and finely distributed the pearlite is distributed accordingly in large patches. This iron had given no trouble with blistering, and is perhaps a very good iron for enameling.

Fig. 4. Graphite is very abundant in large curved crystals as shown. Free cementite occurs very abundantly in groups of minute needles forming narrow bands between the pearlite patches. This sample was taken from a blistered tub.

Fig. 5. Of the same tub showing the patches where the blistering occurred.

Fig. 6. The carbon in this sample is grouped in small round segregations of very minute flakes which, when the surrounding pearlite is deeply etched, show round black patches resembling temper carbon. This arrangement of the carbon gives the sample a mottled appearance. Free cementite occurs in minute needles and narrow bands showing the honeycomb eutectic. The texture is very fine-grained, both cementite and pearlite. This sample had been taken from a tub which blistered badly, and also had a few black glass eyes, so called by the enameler.

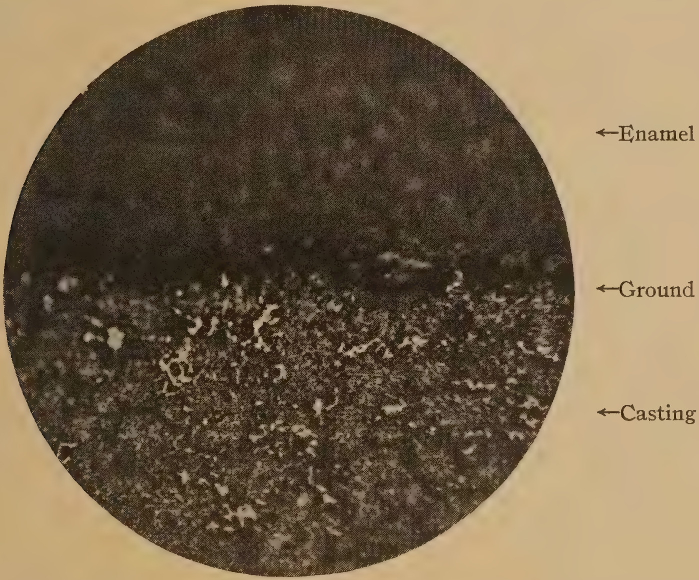

Fig. 7.—Etched, shows enamel vague grey, ground coat (black), cementite needles (white), pearlite (rough grey).

This photograph resembles very closely Figs. 1 and 4.[1]

Fig. 7. This sample was taken from a perfect enameled tub. The sample has abundant graphitic crystals, most of which are arranged with

flat face parallel to the enameled side. Free cementite occurs sparingly and is more abundant toward the enameled side. Texture of the pearlite is coarser than Fig. 6 and about the same coarseness as Fig. 3.

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[1] Manson, *Jour. Amer. Ceram. Soc.*, **5** [11], 809 (1922).

There is no weakness visible between the enamel and ground coat or between the ground coat and iron. This sample is a very good enameling iron.

Summary

Carbon has an intimate connection with the cause of blistering, lifting and in some cases with chipping. This is demonstrated by the chemical analyses as well as by the microphotos.

It is clearly shown that a low combined carbon and an evenly distributed graphitic carbon in very minute state will show no signs of blistering.

It seems that as soon as the combined carbon is high and if temper carbon is present the blistering of the enamel is certain.

The writer is unable to account for the increase of the carbon in the iron due to enameling heat treatment.

The changes in the combined carbon (in the pearlite) during the enameling process mean quite a radical difference in structural composition of the castings, the consequences of which the enamel must bear.

It is necessary to secure as nearly as possible uniform pig and scrap iron, and good quality of a dense and strong structure coke. All finished castings must have a uniform thickness, otherwise chipping, lifting, crazing also pinholes are certain.

The writer wishes to express his thanks to G. B. Schneider, General Manager, for his valuable suggestions and his hearty coöperation, also to C. E. Graham for his assistance in making the analyses and duplicates.

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ORIGINAL PAPERS

TERRA COTTA IN ARCHITECTURAL DESIGN[1]

The Part of the Ceramic Chemist

BY F. S. LAURENCE

ABSTRACT

Emphasis is made of the use of terra cotta as an artistic and decorative material. Its successful use demands an architecturally educated talent and a ceramic chemist who appreciates texture, hue and the required colors. The tendency to employ terra cotta to bring out effects of stone masonry design is shown.

Introduction

Produced as an article of purely commercial manufacture terra cotta is nevertheless an essentially artistic material. Perhaps in no other medium used for the construction of our modern buildings is there to be found in equal degree this marriage of utilitarian and aesthetic character.

Brick, for instance, may be used to fulfil purely practical necessities in construction without regard to aesthetic considerations. It may form the backing of a stone or stucco faced wall and be completely hidden from sight. Brick may on the other hand be used for the exterior facing of a wall whose backing is hollow tile, fulfilling in this case an ornamental or decorative purpose. In a similar way other materials may fulfil this varying function.

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[1] This paper will be presented at the Annual Meeting of the AMERICAN CERAMIC SOCIETY, Columbus, Ohio, Feb., 1925. Recd. Dec. 30, 1924.

Terra Cotta is Decorative

The use of terra cotta however does not carry this divergent possibility. In all cases terra cotta when used must fulfil a decorative function of some character. Even when used in the form of perfectly plain trim for walls of other material it is visible to the sight as a part of the finished surface and therefore enters inevitably into the aesthetic aspect of the building's design. No matter how far removed from the process of art in its production for such purposes its manufacture can never be conceived as entirely apart from and unrelated to the problems of art in the use it must fulfil. Where employed for ornamental enrichment in the various forms of relief modeling which give the final grace to architectural composition its identity as an artistic product becomes even stronger, being so not only from the standpoint of use but in the very method which must be used for its production in that form.

When we enter the field of color effects which are so integrally a part of architectural design its artistic identity receives still further emphasis. From the severest plainness in such commonplace features as sills or ordinary unornamented ashlar to the most ornamental elaboration of decorative form its aspect as color can never be lost sight of, never be disassociated from aesthetic considerations.

Architecturally Educated Talent Essential

It is precisely in this circumstance that the terra cotta industry demands for its successful conduct talent educated in the requirements of architectural design. The governing of manufacture so as to produce an article suited to the purposes of architecture requires this in the business management. The realization of this object in the work performed by various factory departments requires this upon the part of those officials responsible for their direction.[1]

Ceramic Chemist Must Appreciate Textures, Hues and Colors Required

The chemist must be something more than what the term "ceramic chemist" implies in its literal meaning. The most astounding wizardry in the successful production of glazes and colors means nothing if their characteristics of tone, hue and texture are not well related to the problems of use in architecture. Colors and textures may meet every standard of cultivated taste as such and yet be wholly unsuited to the effect which the architect must seek in the final aspect of his building as a work of architecture. Obviously the conduct of experiment in these lines should be guided by knowledge of what can, will or should be used properly in architectural design.

In the terra cotta industry experience has to a large degree removed uncertainty in appropriate aim and our chemists have responded to the needs of our architects with splendid general efficiency. Yet no true friend of the terra cotta industry will maintain that there is not room for betterment in this regard. The ceramic chemist of most value to the terra cotta industry is the one who combines with his scientific proficiency the most intelligent grasp of the requirements of good architectural design in its use of color and material effects generally.

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[1] The aesthetic taste and knowledge of "styles" required, for instance, in directing the modeling department come immediately to mind in this connection.

This does not mean that an actual training in architecture is essential. But study which develops sound discriminative taste in effects of architectural design is a necessity and the question may well be asked, "Are our ceramic schools visualizing correctly the necessary equipment of the ceramic chemist in this regard?" The question of course has relation only to the needs of those ceramic industries whose products are means of realizing aesthetic effects in architecture.

Use of Terra Cotta in Architecture

Tendency in Present Design

In its wide use today, covering almost all classes of building operations throughout the country, terra cotta has been employed chiefly for realizing the effects of stone masonry design. In everything from ashlar to cornices, capitals, brackets, cartouches, medallions and other forms of ornamental elaboration the design in jointing, pattern, profiles and qualities of modeling follows the character of carved stone. Colors and surface textures have likewise repeated this imitative tendency. This is due in great part to the demands of the architectural profession itself whose whole training hitherto has been based on the traditions of masonry design reflected in the architectural monuments of the past.

These architectural monuments of the past came into being, however, when the use of steel for construction was unknown and walls depended for their support upon their mass and weight and the load bearing qualities of material used. The advent of steel as the supporting factor in construction came upon a profession totally unprepared for it in its inherited conceptions of beauty and structural principle. It was scarcely to be expected therefore that a new architectural technique would immediately spring into being more logically adapted to the actual facts of modern construction.

Steel Construction Brings New Treatment

But no such profound change as the introduction of steel in building operations can take place without this altering the entire character of architectural design and ultimately yielding something in style which the world has never before known. The proportional height of our large buildings is one respect in which this mighty change has already manifested itself. One is apt to wonder why the inevitableness of the remaining transformation is not more apparent both to those who design our buildings and those who furnish the materials for their erection. Perhaps an analogy may best be drawn in looking back upon the consequences following the invention of the printing press. Little did the people of that time dream that at one blow there was destroyed the very life of the glorious plastic art which hitherto had been the one great channel through which the thought of the times could best express itself.

In somewhat the same way steel, true to its nature, has stabbed to the heart the beautiful forms of architectural design which we have inherited from the ages gone by. Something else will eventually take their place; not suddenly, but in a process of orderly evolution. Whether this is for the better or worse, time only and the judgment of later ages can tell. In its initial manifestations the change has already come and its full accomplishment may prove swifter than we suspect.

The Responsibility of the Ceramic Chemist

The manufacturer of a ceramic material used in architecture must keep his product well abreast of the developing tendencies in the major art which his effort serves. The ceramic chemist responsible for the production of colors in their various shades, hues, and qualities must know in any event what constitutes an appropriate palette for the architect's use. The construction of such a palette should comprehend effects of color appropriate to the different "periods" or styles in architectural design.

Graduated range of shade in any color should exhibit consistent gradation in intermediates from light to dark and preserve in this range harmonious qualities of hue admitting their being used together without clashing. If, for instance, an architect desiring to use blue in several different shades, were obliged to associate a light "warm," yellow tinged blue, with a slightly darker "cold" blue of raw primary cast, and a still darker shade of blue inclining toward purple, because gradation in this color afforded no other choice, the chances would be very little that they could be worked into harmonious combination. And so throughout the palette in the gradations of all other colors and the possibility of their successful relation, using one or more shades of one color with one or more shades of the other.

A trained aesthetic taste must govern the production of glazes and colors from the standpoint of their harmonious use together in design. Finally, this should embody a selection appropriate in any event to architectural purposes and well related to the corresponding characteristics occurring in other materials used in architecture which may be jointly employed.

Does the academic training of our ceramic chemists cover this important field of study in any particular? Under the current tendency to use more color in architecture it is particularly important that it should. The chemist upon whose creative activity the architect must rely for the material he uses should understand the language of architecture. New problems in the decorative embellishment of our modern buildings are pressing insistently for a satisfying solution. Color is becoming an important factor in these. The ceramic industry holds within the nature of its material unexploited resources of the most promising nature. The National Terra Cotta Society is bending every effort today in its promotional and publicity work toward bringing an appreciation of these to the architectural profession.

The response has been most encouraging and Government statistics of production in the industry during the past several years show marked increases in the use of terra cotta from year to year since 1921. Beautiful examples of architecture, many of them in color, are appearing in all our great cities and are confined to no one section of the country. Most encouraging has been the tendency to recognize the distinctive charms of ceramic material in many of the forms of treatment given to recent executed work. The National Terra Cotta Society is featuring these in recent publications and others yet to appear in the early future.

The opportunities which the future holds are therefore great for the chemist whose initial training or progressive disposition in his post-graduate relation enables him to fulfil the broader requirements of the modern terra cotta laboratory.

National Terra Cotta Society
New York City

THE MAKING OF DOLOMITE BRICK AND A STUDY OF THEIR PROPERTIES[1]

By Andrew I. Andrews,[2] George A. Bole[3] and James R. Withrow[4]

ABSTRACT

This investigation deals with the making and the properties of dolomite brick. A thorough review of the literature shows that there are many improvements possible in the making of dolomite brick and some of the principal faults are pointed out.

In this investigation it was shown that 200-mesh dolomite mixtures of a composition 9–0–6M (9% Fe_2O_3–0% Al_2O_3–6% SiO_2–85% dolomite); 6–3–6M (6% Fe_2O_3–3% Al_2O_3–6% SiO_2–85% dolomite); and 2–4–4M (2% Fe_2O_3–4% Al_2O_3–4% SiO_2–90% dolomite) can, if calcined to cone 20 down, be made into better brick than any previously described. The advantages of this higher fired material are (1) it has been more completely shrunk than that fired at lower temperatures and therefore does not shrink as much when refired in the form of brick, (2) in the use of aqueous binders less trouble is encountered due to slaking than with the lower fired material.

In a continuation of the binder studies a thorough investigation was made of molasses, tar, epsom salts, water and carbonated water. No conditions were found where water, carbonated water, bindex or epsom salts, could be satisfactorily used.

Using 20-mesh (2–4–4M) calcine and 15 and 20% of molasses as a binder it was found that the brick always squatted considerably at about cone 15 down. This was shown to be inherent in the material itself and not due to a migration of any part of the material or a softening of the molasses.

The most successful brick were made using 20-mesh D9–0–6M composition (9% Fe_2O_3–0% Al_2O_3–6% SiO_2–85% dolomite 200-mesh calcined to cone 20 down), plus 13% of a one to three dextrin-water mixture as binder, and 20-mesh S6–3–6M (6% Fe_2O_3–3% Al_2O_3–6% SiO_2–85% dolomite 200-mesh calcined to cone 20 down), plus 12% of a 5% solution of sodium silicate and in each case fired to cones 16 to 18 down. These brick are dense, well shaped and refractory.

Cone fusion temperatures of calcines 9–0–6M, 6–3–6M and 2–4–4M were made in an especially constructed oxyacetylene furnace.

The results of the tests show that the above compositions have cone fusion temperatures above cone 40 (2010°C) down. In connection with this work it was also shown that an electric induction furnace, where graphite is used as the resistor, is not reliable for cone fusion tests due to the strong reducing atmosphere.

In a load test on brick D9–0–6M and S6–3–6M it was found that when they are heated to 1350°C and held at 1350°C for one hour under a load of twenty-five pounds per square inch they show only a small compression. Brick D9–0–6M shows a compression of 3% while S6–3–6M shows a compression of 0.9% neither brick showing any tendency to crack or squat.

In a spalling test these brick (D9–0–6M and S6–3–6M) were shown to possess the characteristic fault of magnesite in that they do not withstand sudden heat change

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[1] Published by permission of the Director, U. S. Bureau of Mines.

[2] Fellow, Ohio State University, 1923–24.

[3] Director, Ceramic Expt. Sta., U. S. Bur. of Mines, Columbus, Ohio.

[4] Head of Department of Chemical Engineering, Ohio State University.

Note: This is the third phase of an investigation by the U. S. Bureau of Mines in coöperation with the Ohio State University Engineering Expt. Station into the possibility of utilizing dolomite as a base material in the manufacture of refractories. The data herein given has been presented to the Graduate School at Ohio State University as a thesis in partial requirement for the Doctor's degree.

without spalling. On heating one hour at 1350°C and then exposing to room temperature they crack badly.

The use of less flux was unsuccessful as the material thus prepared shows strong hydration which is fatal in that it causes the material to disintegrate.

Dolomite compositions 9–0–6M, 6–3–6M and 2–4–4M, flux violently with silica and fire brick but are inactive toward magnesia and chrome brick. It is, however, possible to burn the dolomite on fire clay brick if a thick layer of magnesia brick grog is used.

Since it is necessary to grind the dead-burned dolomite before it can be made up into brick it is necessary to know the relative tendency toward slaking of the various size particles. It was found that the finer the calcined dolomite is ground the more rapidly the slaking takes place and that it is in some cases very appreciable for 20-mesh material as used in making brick.

Introduction

Since magnesite suitable for making refractory brick is an expensive raw material and dolomite is relatively cheap, it would be a great saving to the industries using basic refractories if dolomite could be substituted for magnesite.

Robson and Withrow[1] have made a survey of the use of ferric oxide (Fe_2O_3), alumina (Al_2O_3), and silica (SiO_2) as fluxes for dead-burning dolomite and have produced promising compositions.

The object of this work is to investigate the following: (*a*) the use of the compositions suggested by the previous work in the making of dolomite brick, (*b*) the study of the effects of temperature on the properties of the brick to determine the optimum firing temperature including a study of the cause of "slumping" of dolomite brick during firing, (*c*) the thorough study of various binders and their advantages or disadvantages; (*d*) an investigation of the properties of the dolomite brick relative to their applicability to service conditions.

Experimental

Preliminary Work A very pure grade of dolomite of the Niagara formation obtained from Cedarville, Ohio, was used in this work. It was crushed in a jaw crusher, put through rolls and finally ground in a dry pan to pass 100-mesh. A second batch was pulverized by means of a Jeffrey hammer pulverizer and then ground in a dry pan to pass 200-mesh screen. The chemical analysis of this dolomite, based on the dry weight (110°C), is given in the following table (page 86).

The true specific gravity determined by the kerosene-pycnometer method, of dolomite batch No. 2 is 2.83. Since there is very little differ-

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[1] J. T. Robson and J. R. Withrow, "The Dead Burning of Dolomite," *Jour. Amer. Ceram. Soc.*, 7 [1], 61; [2] 141; [3], 207; [4], 300 (1924).

		Batch No. 1	Batch No. 2
Silica	(SiO_2)	0.4	0.38
Aluminum oxide	(Al_2O_3)	.5	.5
Iron oxide	(Fe_2O_3)	.5	.4
Calcium oxide	(CaO)	30.2	30.3
Magnesium oxide	(MgO)	21.8	21.7
Sodium oxide	(Na_2O)	trace	trace
Sulphur trioxide	(SO_3)	none	none
Carbon dioxide		46.8	47.1
		100.2	100.48
Loss on heating to 105°C		.11%	....
Loss on heating to 110°C		....	.24%

ence in the composition of the two dolomites, no distinction will be made in future work.

The following fluxes with their typical analyses are:

Alumina	
Al_2O_3	99.99
SiO_2	.001
FeO	.003
CaO	trace
Cl	trace
SO_3	trace

Ferric oxide	
Fe_2O_3	99.99
FeO	none
SO_3	trace

Flint	
SiO_2	99.80
Al_2O_3	.18
Fe_2O_3	.01
CaO	none
MgO	none

Iron ore	
Fe_2O_3	88.88
SiO_2	6.68
Al_2O_3	2.01
FeO	0.00

Bauxite	
Al_2O_3	50.20
Fe_2O_3	3.80
SiO_2	21.00

Sodium silicate	
Na_2O	25.13
SiO_2	24.95
H_2O	49.38

The binders in each case will be described in detail when used in connection with the investigation.

Key to Compositions and Definitions

The numbers representing the sample indicate the composition of the flux. The first number represents the percentage ferric oxide, the second number alumina and the third number silica. Letters are used to indicate various modifications. Thus, a composition marked 2–4–4 represents 2% Fe_2O_3, 4% Al_2O_3, 4% SiO_2 and 90% dolomite. 2–4–4M indicates that the composition is the same as above but that 200-mesh material was used in making up the composition for calcining. Other modifications will be given later and explained when first used.

Flux. By the term flux in this paper, it will be understood to mean constituents such as Fe_2O_3, Al_2O_3 and SiO_2 which with part of the dolomite forms the glassy portion of the body.

Binder. By the word binder it will be understood that this is a material used to hold the particles of material together in the green or lightly fired state.

Cones. Orton standard pyrometric cones have been used throughout this work.

Apparent Porosity. Refers to open pore space.

True Porosity. Refers to open plus closed pore space.

Preliminary Investigation

The properties of the brick made according to Robson and Withrow[1] were studied and the feasibility was determined of using commercial material such as iron ore, bauxite and kaolin in place of the pure oxides as fluxes. Cedarville dolomite, 100-mesh, was thoroughly mixed with the fluxes appearing in the following table by means of grinding the batch together.

Brick	2–2–4	2–2–4E	2–2–4C	6–3–6	6–3–6E	9–0–6	9–0–6E
Dolomite	90	90	90	85	85	85	85
Fe_2O_3 C.P.	2	..	..	6	..	9	..
Al_2O_3 C.P.	4	..	..	3	..	0	..
SiO_2 C.P.	4	4	4	6	6	6	6
Iron ore (Fe_2O_3)	..	2	2	..	6	..	9
Bauxite (Al_2O_3)	..	4	..	..	3	..	..
N. C. kaolin	..	..	4	..	..	..	..

When commercial materials were used, corrections were made for the impurities. For illustration: the iron ore contains Fe_2O_3, Al_2O_3 and SiO_2. The amount of ore added will be sufficient to bring the Fe_2O_3 content of the mix up to the required percentage and the amount of Al_2O_3 and SiO_2 to be added will be diminished by the amount contained in the iron ore. Corrections were also made for hygroscopic water.

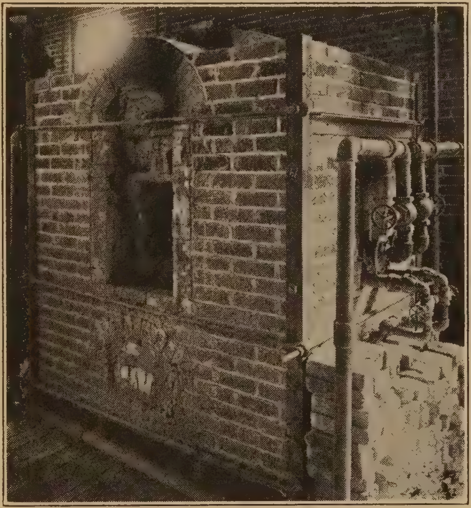

FIG. 1.

After thoroughly mixing the constituents by putting them through the disc pulverizer, sufficient water was added to make them moldable. They were then made into briquettes (1 x 2 x 4″) and dried at 110°C. They were set in the down-draft kiln (Fig. 1) on fire brick dusted over with 20-mesh magnesia brick grog. It was necessary to make two firings as all the batch could not be set in the kiln at one time. One-half of each composition, however, was included in each firing.

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[1] J. T. Robson and J. R. Withrow, *loc. cit.*

In the second firing the briquettes were set on magnesia brick as they fluxed considerably with the fire brick dusted over with magnesia.

The time-temperature curves are shown on Fig. 2, semi-oxidizing conditions being maintained throughout the firing.

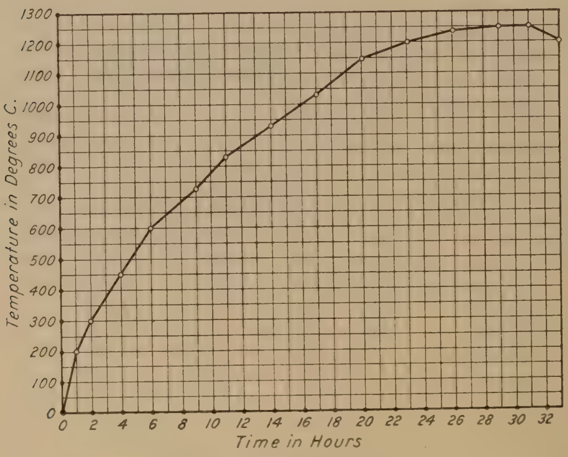

FIG. 2.—Brick firing I–II.

These temperatures were measured by means of a platinum, platinum-rhodium thermocouple extending through the back of the kiln and about four inches through the inside wall into the combustion chamber. In each case, cone 17 was down and cone 18 standing at the end of the burn. The kiln was allowed to cool normally, requiring about two days.

Results of Calcination. The briquettes showed about 40% volume shrinkage, were very hard and black in color shading to a brown on the interior especially in the cases of low iron content.

The briquettes were crushed in a jaw crusher and ground in a disc pulverizer to pass 20-mesh. The screen analysis of this material was as follows:

	Residue						
Calcine mesh	2–4–4	2–4–4E	2–4–4C	6–3–6	6–3–6E	9–0–6	9–0–6E
20	0.0	0.0	0.0	0.0	0.0	0.0	0.0
48	15.0	10.0	10.3	18.0	16.1	21.1	14.6
100	64.8	70.7	67.2	70.3	61.9	62.3	72.4
Fines	20.2	19.3	22.5	11.7	23.0	16.6	13.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

This material was next made up into brick as follows:

Brick M[1]2–4–4. To 3250 grams of the calcined 2–4–4 composition 813 grams (20%) of molasses were added and thoroughly mixed by hand. It was then pressed into a brick at 500 lbs. pressure per square inch and allowed to air dry for two days.

Brick M2–4–4E. To 3244 grams of 2–4–4E dead-burned composition,

---

[1] The letter preceding the composition number indicates the binder used as M for molasses, S for sodium silicate, D for dextrin.

811 grams (20%) of molasses were added, mixed and a brick molded, pressed and dried as above.

Brick M2–4–4C. To 3407 grams of 2–4–4C (dead-burned), 852 grams (20%) of molasses were added and a brick made as above.

Brick S6–3–6. To 3360 grams of 6–3–6 (dead-burned), 840 grams (20%) of a 5% sodium silicate solution were added, mixed and pressed into a brick by hand. On drying at 110°C this brick cracked badly. It was repressed with 20% more of the sodium silicate solution and dried at room temperature but again it cracked. It was then repressed with 20% more of the sodium silicate solution and subjected to a humid atmosphere for drying but this caused a complete disintegration. It was likely that the cracking was due to the slaking of the lime which caused a swelling of the brick and resulting failure.

Brick S6–3–6E. To 2800 grams of dead-burned 6–3–6E composition, 700 grams (20%) of a 5% sodium silicate solution were added, mixed and pressed into a brick by hand. As with brick 6–3–6, this brick could neither be dried at 110°C nor in room conditions.

Brick D9–0–6. To 3045 grams of dead-burned 9–0–6 composition, 455 grams (13%) of a one to three dextrin-water mixture were added, mixed by hand and pressed into a brick at 500 pounds per square inch pressure. It was dried at 110°C but cracked badly.

Brick D9–0–6E. To 3045 grams of dead-burned 9–0–6E composition, 455 grams (13%) of a one to three dextrin-water mixture were added, mixed, pressed and dried as above but again the brick cracked badly.

Drying Results

1. Brick M2–4–4, M2–4–4E and M2–4–4C dried successfully under room conditions.
2. Brick S6–3–6 and S6–3–6E using 20% of a 5% sodium silicate solution could not be dried under room conditions nor at 110°C without cracking.
3. Brick S6–3–6 could not be dried in a humid atmosphere without disintegrating completely.
4. Brick D9–0–6 and D9–0–6E using 13% of a one to three dextrin-water mixture could not be dried at 110°C without cracking.

Brick Firing No. 1

Since the brick S6–3–6, S6–3–6E, D9–0–6 and D9–0–6E could not be dried successfully, they were not included in this firing. The following bricks M2–4–4, M2–4–4E and M2–4–4C were set on end on magnesia brick dusted over with 20-mesh magnesia brick grog, in a round down-draft kiln. The dolomite brick were protected from the direct flame

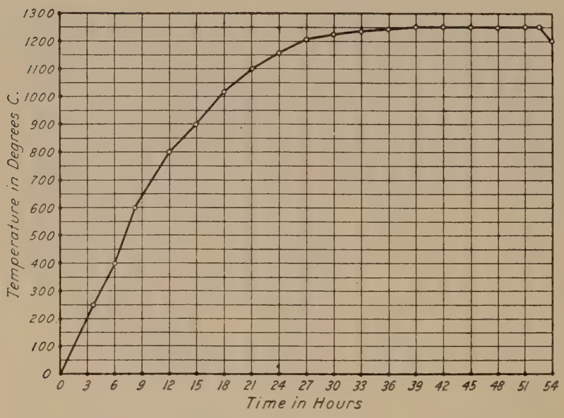

FIG. 3.—Brick firing I.

by a checker of fire brick. The time-temperature curve is shown in Fig. 3, cone 15 being down and cone 16 standing at the end of the forty-five hour firing. The kiln was cooled slowly requiring about two days.

Results of Brick Firing No. 1

All three bricks M2–4–4, M2–4–4E, and M2–4–4C (Fig. 4), had squatted badly, being about one-half inch wider at the base than at the top. There were many small cracks at the base and the brick had sagged over to such an extent as to flux with the fire clay brick standing about one inch away. The characteristic properties of these brick are shown in the above table.

Property	M2–4–4	M2–4–4E	M2–4–4C
Color	black	black	black
Shape	Squatted and warped	Squatted and warped	Squatted and warped
Linear shrinkage	17.1	17.2	17.2
Apparent porosity	10.5	10.7	9.9
Apparent density	2.92	2.87	2.96
Weight	2965 grams	2980 grams	3047 grams

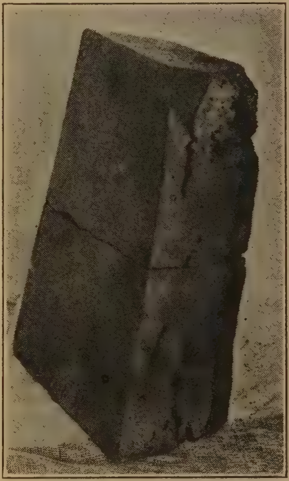

FIG. 4.—Brick M2–4–4.

Conclusions. Since these brick have an excessive shrinkage, low porosity and a tendency to squat on firing to cone 15 down, they would not serve satisfactorily as a refractory. The excessive shrinkage has a tendency to crack and warp the ware and presents commercial firing problems, the low porosity shows them to be very vitreous which tends to cause spalling.

Calcination No. 2

Since none of the brick thus far made stand up to the requirements of a basic refractory it was decided to make several modifications in the process of fabrication. In the first place it was decided to use 200-mesh material for calcining in order to get more intimate contact between the particles, more complete uniformity and therefore more efficient dead-burning. This would likely do away with some of the slaking action of the ground calcine. Robson and Withrow suggested that the nature of this dead-burning was that of an envelope of flux over the lime particles. Therefore, the smaller the lime particles the more efficient this dead-burning ought to be. In addition to the above modification, it was decided to calcine the material at cone 20 instead of cone 17. This would decrease the shrinkage of the material when it is later made up into brick and fired at a lower temperature.

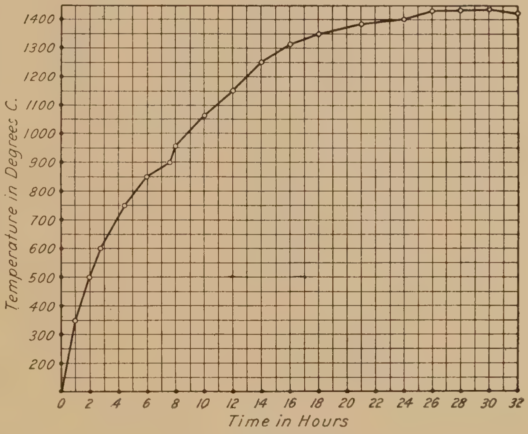

Fig. 5.—Firing II.

Ten kilos each of 2–4–4, 6–3–6, and 9–0–6 compositions were made up with the above modifications. 200-mesh material[1] was used and the calcination was carried to cone 20 down, the time-temperature curve being shown in Fig. 5. This dead-burned material was crushed in a jaw crusher and ground to 20-mesh in a disc pulverizer.

	Per Cent Residue		
Mesh	2–4–4M	6–3–6M	9–0–6M
20	2.0	2.1	3.8
35	39.8	45.0	41.0
48	14.0	9.3	11.1
65	5.8	.2	7.7
100	8.7	8.4	7.2
150	5.2	3.8	3.6
200	5.2	7.0	3.8
Fines	19.2	24.0	21.8
Total	99.9	99.8	100.0

The above table shows the screen analysis of the dead-burned dolomite.

Study of Firing Temperature

Thus far, no systematic study has been made on the effect of firing temperature on the brick. This was therefore the next problem undertaken.

---

[1] Batches in which 200-mesh material was used and which were fired to cone 20 down, will be designated by following the composition number by the letter M. Illustration: 2–4–4 composition in which 200-mesh material was used and calcined to cone 20 down, will be 2–4–4M.

Briquettes were made up of 2–4–4M, 9–0–6M and 6–3–6M composition using molasses, dextrin and sodium silicate respectively, as binders. For 2–4–4M, 15% of molasses was used as the binder. Ten per cent of molasses has been shown to be insufficient and it is desired to use the minimum amount which will serve the purpose. For 9–0–6M composition, 10% of a one to three dextrin-water mixture was used and for 6–3–6M, 10% of a 5% sodium silicate solution was used. These briquettes were molded by hand and had dimensions of 1 x 2 x 4 inches. They dried well and were very firm and strong. These briquettes were then placed in the kiln on end, on magnesia brick dusted over with magnesia brick grog. Cone plaques were placed beside each test piece and the tests were well protected from the direct action of the flame. Draw trials were taken at regular intervals as shown by the attached table, the test pieces being immediately buried in powdered magnesia to prevent too rapid cooling and spalling. None of these briquettes showed any decided spalling.

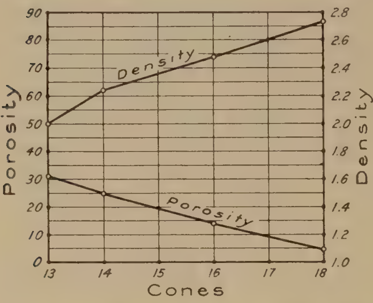

Fig. 6.—Study of firing temperature 9–0–6M.

The apparent porosity and density were determined from data obtained as follows:

1. Weight of briquette dry.
2. Weight of briquette after soaking in kerosene for two days.
3. Weight of briquette suspended in kerosene.
4. Specific gravity of kerosene.

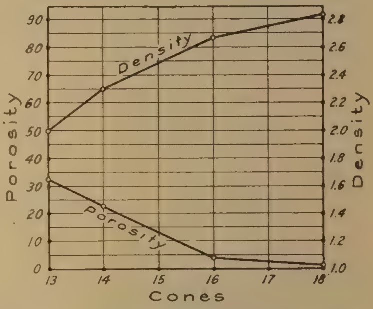

Fig. 7.—Study of firing temperature 6–3–6M.

The specific gravity of the kerosene was determined by the pycnometer method.

The following table (page 93) shows the results of the tests.

These results as shown by the curves in Figs. 6, 7 and 8 give the following information:

1. With increase of temperature there is increased shrinkage.
2. With increase in firing temperature, the apparent porosity becomes less.
3. With increase in firing temperature, the density becomes greater.

Compn.	Cone	Color	Shape	Linear shrink.	Odor	Strength	Apparent porosity	Sp. gr.
2–4–4M	4	green	OK	none	molasses	dusty	crumbled	....
2–4–4M	6	green	OK	none	molasses	dusty	crumbled	....
2–4–4M	8	green	OK	none	molasses	dusty	crumbled	....
2–4–4M	10	grey	OK	none	molasses	dusty	crumbled	....
2–4–4M	12	grey	OK	none	molasses	dusty	58.6	1.37
2–4–4M	14	grey	OK	none	molasses	weak	38.6	1.89
2–4–4M	15	black	OK	10%	molasses	good	38.0	1.99
2–4–4M	16	black	OK	12%	slight	good	35.2	2.07
2–4–4M	17	black	warped	15%	none	good	31.4	2.11
2–4–4M	18	black	bad	17%	none	v. strong	22.3	2.41
2–4–4M	20	black	bad	....	....	v. strong	13.4	2.64
9–0–6M	13	black	good	3%	....	fragile	30.5	2.10
9–0–6M	14	black	good	4%	....	fragile	25.3	2.33
9–0–6M	16	black	good	8%	....	fragile	14.4	2.59
9–0–6M	18	black	good	12%	....	strong	5.0	2.83
6–3–6M	13	black	good	2%	....	fragile	32.8	2.00
6–3–6M	14	black	good	3%	....	fragile	26.0	2.30
6–3–6M	16	black	good	8%	....	fragile	8.3	2.68
6–3–6M	18	black	good	12%	....	strong	1.7	2.83

The apparent porosity, however, is not complete information due to the fact that there may be a great number of closed pores which do not appear in an apparent porosity determination. The true porosity was therefore determined. In order to do this, it was necessary to get the true density of the material. This was done by the pycnometer method using kerosene. In a calibrated pycnometer, the density of the kerosene to be used was accurately determined. About twenty grams of the calcined dolomite was then transferred to the weighing bottle and accurately weighed. The bottle was then filled with the kerosene and a new weighing made. The following information was then known:

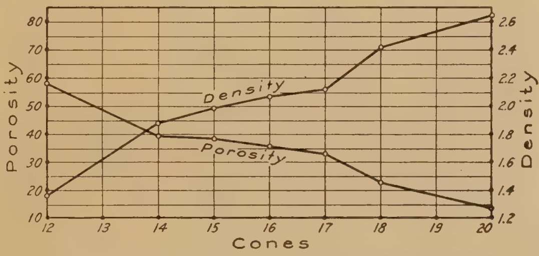

Fig. 8.—Study of firing temperature 2–4–4M.

1. The weight of exactly 50 cc. of kerosene.
2. The weight of the dolomite.
3. The weight of the dolomite plus enough kerosene to make up 50 cc. of volume.

Results show the following densities for the three calcines:

Calcine	Density
2–4–4M	3.31
9–0–6M	3.44
6–3–6M	3.39

It is now possible to calculate the true porosity of the briquettes and also the closed pore space as follows:

D = Density of material
d = Bulk density of briquettes
D : 100% of solid :: d : actual per cent of solid
True porosity — apparent porosity = closed pore space.

The following table[1] shows the results obtained:

Cone	D	d	Apparent porosity	True porosity	Closed pore space
2–4–4M					
12	3.31	1.37	58.6	58.6	0.0
14	3.31	1.88	38.6	42.9	4.3
15	3.31	1.99	38.0	39.9	1.9
16	3.31	2.07	35.2	37.5	2.3
17	3.31	2.11	31.4	36.3	4.9
18	3.31	2.41	22.3	27.2	4.9
20	3.31	2.64	13.4	20.3	6.9
9–0–6M					
13	3.44	2.10	30.5	39.0	8.5
14	3.44	2.33	25.3	32.3	7.0
16	3.44	2.59	14.4	27.6	13.4
18	3.44	2.83	5.0	17.7	12.7
6–3–6M					
13	3.39	2.00	32.8	41.0	8.2
14	3.39	2.30	26.0	32.0	6.0
16	3.39	2.68	8.3	21.0	12.7
18	3.39	2.83	1.7	26.5	24.8

From the above results it may be concluded:

1. With increase in temperature, the true porosity becomes less.
2. With increase in temperature the closed pore space becomes greater.

Since in the above results the briquettes do not reach a maximum shrinkage at any of the temperatures used and since porosity seems to be still changing, it was decided to fire these briquettes to higher temperatures.

For this purpose, a surface combustion furnace was used (Fig. 9) and the temperatures were determined with an optical pyrometer. The test pieces were made up similar to the above briquettes but one-inch cubes were used instead of pieces 1 x 2 x 4 inches as in the above work. This was necessary due to the fact that the heating chamber was very small. These briquettes were placed on a graphite plate, three at a time, 2–4–4M, 9–0–6M and 6–3–6M and heated to temperatures varying from 1575°C to 1800°C. The length of time that the briquettes were held at this temperature varied from thirty to forty minutes and the temperature recorded was the average of a number taken during this period. After firing 2–4–4M was most vitreous, 6–3–6M next and 9–0–6M the least. The following table shows the properties of these various briquettes:

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[1] The following figures have been calculated on the assumption that the density does not change with firing temperature.

Comp.	Cone	Temperature	Density	Porosity
2–4–4M	22	1575	2.94	0.818
2–4–4M	23–24	1604	2.91	1.28
2–4–4M	26	1663	2.60	2.67
6–3–6M	22	1575	3.08	4.26
6–3–6M	23–24	1604	3.00	1.50
6–3–6M	26	1663	2.94	2.53
6–3–6M	27–28	1675	2.79	2.39
9–0–6M	22	1575	3.10	1.98
9–0–6M	23–24	1604	3.34	2.21
9–0–6M	26	1663	3.03	1.92
9–0–6M	27–28	1675	3.00	2.69

The following were heated to 1800°C but the pieces had so squatted and fused together that they could not be identified:

	34	1800	2.49	1.77
	34	1800	3.05	0.81

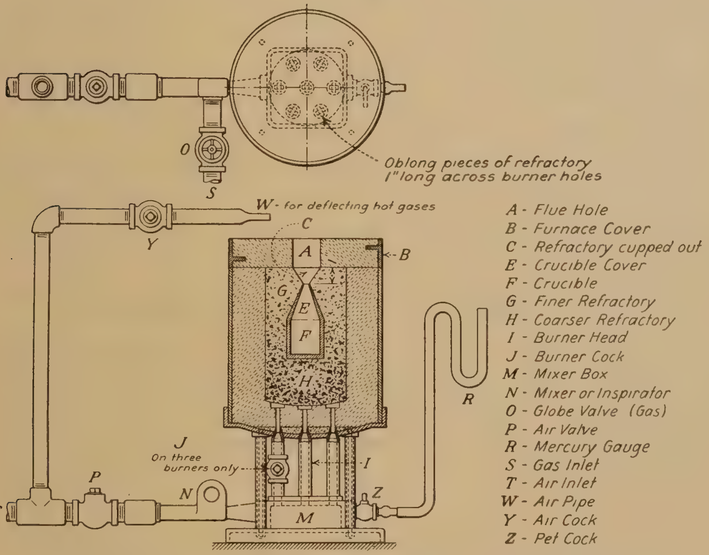


FIG. 9.—Cone fusion furnace (The Surface Combustion Co.)
Date, April 11, 1922. Scale: 3″ = 1 ft.

The above data show that at high temperatures the porosity is low and the specific gravity is greater than at the lower temperatures. The density does not seem to have reached a maximum even at cones 27–28. The shrinkage is progressively greater from the lower to the higher temperatures.

The conclusions of this work on firing temperatures are as follows:

1. It is not desirable to fire dolomite bodies below cone 14.

2. As the firing temperature increases, the porosity decreases.

3. As the firing temperature increases, the density increases.

4. If the briquettes are fired to cones 27–28, they do not reach the true density of the material.

5. The three compositions in order of their vitrification at high temperatures (1575–1675°C) are: 2–4–4M greatest, 6–3–6M next, and 9–0–6M least vitrified.

6. With increase in temperature, shrinkage increases.

7. The closed pore space increases with firing temperature.

8. The true porosity decreases with firing temperature.

9. 2–4–4M appears to have (below cone 20), greater porosity and lower specific gravity than 6–3–6M and 9–0–6M, while 9–0–6M has less porosity but about the same density as 6–3–6M.

10. 2–4–4M has less closed pore space than 9–0–6M and 9–0–6M has less than 6–3–6M. (Closed pore space is an advantage over open pore space as there is less chance for corrosive action.)

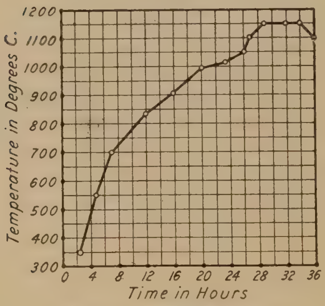


Fig. 10.—Brick firing II. Cone 14 down.

11. The next brick firing was at cones 14, 16, and 18 to determine exactly which is the best firing temperature since results on briquettes are not truly comparable to those which may be obtained with standard sized brick.

Firing Temperatures for Standard Sized Brick

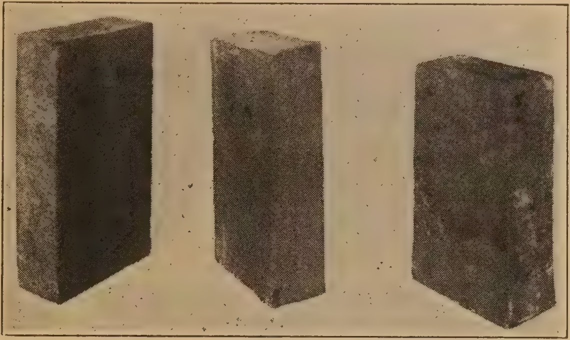
Since the firing temperature as determined by briquettes is not conclusive, it was necessary to make a further study with standard sized brick. Another batch of calcine was therefore made up and as described on page 88, was ground to pass 20-mesh. The screen analysis was as follows:

	Residue		
	Per cent		
Mesh	2–4–4M	6–3–6M	9–0–6M
20	0.0	0.0	0.0
35	38.5	43.2	42.6
48	16.0	7.9	8.9
65	7.8	5.4	9.1
100	8.7	8.9	7.9
150	5.8	4.2	4.3
200	5.0	7.1	4.0
Fines	18.2	23.3	23.2
	100.0	100.0	100.0

This material was made up into brick as follows:

Brick M2–4–4M To 3000 grams of 2–4–4M (dead-burned), 15% of molasses was added and thoroughly mixed by hand. It was then pressed into a standard sized brick at 500 pounds pressure per square inch and dried in the air for two days.

Brick S6–3–6M To 3000 grams of 6–3–6M (dead-burned), 13% of a 5% solution to sodium silicate was added and thoroughly mixed. It was then pressed into a brick by hand and dried for twenty-four hours at 110°C. It dried very well, showing no cracks although weak before drying.



D9–0–6M S6–3–6M M2–4–4M

Fig. 11.

Brick D9–0–6M

To 3000 grams of 9–0–6M (dead-burned), 13% of a one to three dextrin-water mixture was added and after mixing the batch, was pressed into standard sized brick at 500 pounds pressure per square inch. This brick dried very well at 110°C in twenty-four hours.

Brick D9–0–6 To 3000 grams of D9–0–6 (dead-burned), which had cracked badly with dextrin as a binder, 750 grams of molasses was mixed. This mixture was pressed into a brick at 500 pounds pressure per square inch. It dried well at ordinary temperatures.

These brick, S6–3–6M, D9–0–6M and M2–4–4M were then set on end on magnesite brick dusted over with magnesite brick grog. A checker of fire brick was built around each dolomite brick to protect it from the direct action of the flame. The round down-draft kiln was used. The time-temperature curve is shown on Fig. 10. The brick were fired to cone 14 down in thirty-four hours. Cone plaques placed in various locations in the kiln showed that the heating was very uniform

Results of Brick Firing No. 2

Brick D9–0–6M and S6–3–6M were very firm and strong with sharp edges and little tendency to warp or squat. Brick M2–4–4M, however, squatted slightly, being a little larger at the base than at the top but was otherwise very good. The properties of the brick were carefully determined as follows:

The volume was calculated by means of five linear measurements in each direction, averaged, and the results multiplied by each other.

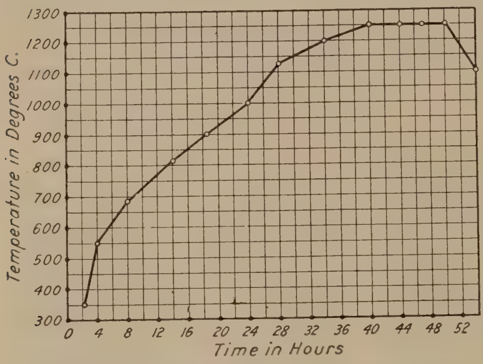


FIG. 12.—Brick firing III. Cone 16 down.

Length x width x thickness = volume.

The density was determined by dividing the weight by the volume:

$$\text{Density} = \frac{\text{volume cc.}}{\text{weight gms.}}$$

The linear shrinkage was determined by measuring the distance between points represented by the intersection of two lines. The original distance between these points, minus the final distance, divided by the original distance and multiplied by one hundred equals the percentage linear shrinkage.

The apparent porosity of these brick was determined by means of an air expansion brick porosimeter.[1]

Brick Firing No. 3

After these tests were completed, the brick M2–4–4M, D9–0–6M and S6–3–6M were reset in the kiln as for brick firing No. 2. They were fired to cone 16 down in fifty hours according to the time-temperature curve, Fig. 12. The kiln was again allowed to cool slowly and the brick were again tested as after brick firing No. 2. M2–4–4M had squatted slightly more after firing to cone 16 than cone 14 down. The appearance of D9–0–6M and S6–3–6M was not appreciably changed.

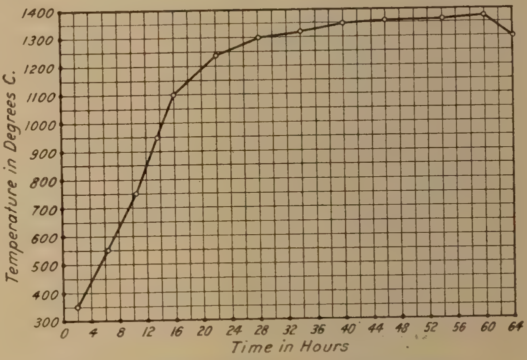


FIG. 13.—Brick firing IV. Cone 18 down.

Brick Firing No. 4

When the tests on brick M2–4–4M, D9–0–6M and S6–3–6M were completed, they were again set in the kiln as for brick firing No. 2. This firing was carried to cone 18 down in sixty hours, the time-temperature curve being shown on Fig. 13. The kiln was slowly cooled for three days and the brick removed and tested as in the two previous firings. Brick M2–4–4M showed decided squatting but D9–0–6M and S6–3–6M were fairly good, showing, however, a slight tendency to squat.

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[1] E. E. Pressler, *Jour. Amer. Ceram. Soc.*, **7** [3], 154 (1924).

The results from the tests on bricks M2–4–4M, D9–0–6M and S6–3–6M when fired to cones 14, 16 and 18, are shown in the following table:

	M2–4–4M Molasses			S6–3–6M Sodium silicate		
Cone	14	16	18	14	16	18
Color	black	black	black	black	black	black
Linear shrinkage	6	15	19	3	9	12
Weight	2939	2908	2819	2948	2942	2791
Volume	1386	1077	973.7	1245	1107	1112
Bulk density	2.12	2.70	2.89	2.33	2.66	2.51
Porosity	35.84	15.23	10.86	30.61	20.33	25.07

	D9–0–6M Dextrin		
Cone	14	16	18
Color	black	black	black
Linear shrinkage	0	4	7
Weight	2905	2898	2887
Volume	1304	1166	1020
Bulk density	2.26	2.48	2.83
Porosity	35.48	27.79	15.15

All three of these brick are very good, the only great fault is that brick M2–4–4M shows some squatting. Each brick is very hard, firm and strong.

When fired to cone 14 down, the porosity 30.61 to 35.84% is too great for a refractory brick. It gives too much surface to the penetration and action of slag. At cone 16 the porosity 15.23 to 27.79 is better but at cone 18, a porosity of 10.86 to 25.07 is more desirable. The shrinkage of M2–4–4M is very great at any temperature above cone 14 while for brick D9–0–6M and S6–3–6M, the shrinkage even at cone 18, while high, is not excessive.

Brick M2–4–4M shows a sudden loss in weight of 89 grams (about 3%), between cones 16 and 18. This loss is likely due to volatilization of some of the more volatile constituents.

Brick S6–3–6M also shows a sudden loss in weight of 151 grams (5.1%), a slightly lower density and a decided increase in porosity. This again appears to be a case of volatilization, since if a particular constituent distils out of the mass, it would likely leave it porous, lower its bulk density and also cause a loss in weight.

Brick D9–0–6M does not show any similar decided variation.

Conclusion on Brick Firing

1. Brick D9–0–6M has the least shrinkage and when fired to cone 18 down, has a porosity of 15.15% which is neither excessive nor so low as to make the brick sensitive to heat change. It is concluded as being the best brick thus far produced.

2. Brick S6–3–6M has a permissible shrinkage of 9% at cone 16 down and if this temperature treatment is used it has a satisfactory porosity of 20.33%. It is a very good brick and can be considered to be almost as good as brick D9–0–6M.

3. Brick M2–4–4M is much less satisfactory than D9–0–6M and S6–3–6M due to the squatting, high shrinkage and low porosity.

The most desirable temperature for firing brick M2–4–4M is cone 14 down; for brick S6–3–6M, cone 16 down and D9–0–6M, cone 18 down. Due to shrinkage and squatting these brick will not meet the requirements of industrial use above the temperature at which they are fired.

(To be continued)

BETTER TERRA COTTA SLABS[1]

By F. B. Allen[2]

ABSTRACT

Terra cotta slab problems are discussed as to (1) refractoriness, (2) mechanical strength, (3) accurate dimensions, (4) temperature changes, (5) spalling, (6) thermal conductivity, and (7) abrasion. Mixes of two experimental bodies are given. The second consisting of 30 grog, 15 clay of low plasticity and 55 bond clays gave satisfactory results.

Introduction

The improvement of his product is the desire and aim of every honest manufacturer. He is constantly on the lookout for means, either of a mechanical or constitutional nature, whereby he may be enabled to attain this end. But before making any fundamental changes he must be reasonably certain that they will produce the desired result and that they are of sufficient importance to warrant such changes. As we all know, basic changes are generally expensive.

The Terra Cotta Slab Problems

Our understanding of this problem is as follows:

High Refractoriness This is not essential. The body must be sufficiently refractory to carry the load without warpage or deformation. As most terra cotta manufacturers are firing to cone 8 or less, this particular feature comes within easy range.

Mechanical Strength This is very important, not because of the load under fire (this is not severe) but chiefly because of the handling of the slabs in setting and drawing the kiln. A 3 x 24 x 24-foot slab made by the soft-mud process, weighs approximately one hundred and twenty pounds. Unless the kiln setters and drawers are conscientious and careful, much breakage is produced in these operations. It is obvious that a strong and tough slab will stand rough handling much better than one which is weakly bonded.

Accurate Dimensions These are desirable. Extreme accuracy is not worth attainment, but slabs measuring within reasonable limits are easy to produce. Such slabs are placed rapidly, produce an even bearing, and are therefore more economical.

Temperature Change While the rate of temperature change under normal conditions is low, a slab, able to stand sudden thermal changes, will often be advantageous.

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[1] Recd. Dec. 27, 1924. Presented at the Atlantic City meeting, Feb., 1924. (Terra Cotta Division.)

[2] Ceramic Engineer, M. D. Valentine & Bro. Co., Woodbridge, N. J.

Spalling Slabs should be non-spalling and free from "spit-out" for evident reasons.

Thermal Conductivity A slab should have a relatively high thermal conductivity to aid in the even distribution of heat and uniformity of firing.

Abrasion While a slab is not subjected to any abrasive action under fire, nevertheless in handling into and out of the kiln considerable rubbing takes place. A slab should be sufficiently tough to resist this action.

Effect of Materials

These various characteristics are attained through the proper selection of materials and methods of manufacture.

Refractoriness is controlled through the clay bond and also the grog. In this particular problem a considerable range of clays is available. One limiting factor is that of the original firing. It is safe to assume that if the slabs come from the kiln having received a normal cone 12–13 firing, true and accurate, they will stand in this respect the lower terra cotta firing.

Mechanical strength and toughness is a question of bonding clays and size of grog. There appears to be a lack of agreement among the different experimenters and users as to the effect of size of the grog. Some have obtained results which indicate that a stronger slab is produced by using grog of varied sizes. Others have found that in their particular problem, large coarse grog gives better load carrying qualities and longer kiln life. Professor Brown[1] says in reference to a sagger mixture, "In a sagger mixture in which there is a preponderance of large sized grog particles, the spaces between the grains are filled with the bond clay which, in vitrifying, allows the particles of grog to slide upon each other. Instead of having a skeleton of grog particles touching at many points and held together by the bond clay we have a matrix of bond clay in which are embedded the grog particles and the bond clay becomes the predominating factor in the behavior of the mixture. If there is a preponderance of large sized grog particles there will be an excess of bond clay between the grog grains, and the bond clay having a greater shrinkage than the grog, decreases in volume and pulls away from the grog particles causing a strain and producing the small cracks which are bound to decrease the mechanical strength of the sagger."

This statement coincides with our views. But then, in a recent article

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[1] Geo. H. Brown, "Notes on Sagger Clays and Mixtures," *Jour. Amer. Ceram. Soc.*, **1** [10], 716(1918).

W. S. Williams[1] found that "under comparable conditions as met in large scale factory practice, the practical elimination of grog particles finer than 40-mesh has resulted in increased service from refractory clay, glass-drawing pots."

It is rather difficult to understand the high mechanical strength of a coarse grog body. One must conclude that the bond clay in this case must be selected with great care.

Spalling appears to be a function of the thermal expansion and contraction of the body. Open firing clays have less tendency to spall because of their greater surface of radiation. Howe and Ferguson[2] found that the reduction of a plastic dense firing clay to 20% of the batch and a corresponding increase in the open firing clay entirely eliminated spalling.

As to thermal conductivity, in general, the denser the slab, the higher will be the rate of conduction. Inasmuch as it is desirable for other reasons to have a hard and comparatively dense slab, a mixture of good thermal conductivity will also give the other requisite properties.

Experimental Bodies

The clays used in the following mixtures are all produced in the Woodbridge district. Broadly, they are all refractory clays, differing chiefly in the degree of plasticity. The mixtures are produced on the volume basis, tempered by the ring pit method and molded by hand. The water content is just sufficient to render the mud to the "soft" condition.

For quite a period of time the following mixture was used for these slabs.

26	grog
50	clay of low plasticity
24	bond clays
100	

In general, terra cotta slabs of this mixture gave only fair results. They were accurate and true, but were too refractory for the service required.

The first change made in the above consisted in raising the grog to 35%. Also the grog was selected so that there was more variation in size than in the former mixture. The proportion of the grog was increased with a corresponding decrease in the proportion of the clays of low plasticity. The bond clays remained as before.

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[1] W. S. Williams, "Effect of Various Sizes of Grog Particles on Clay Pots," *Jour. Amer. Ceram. Soc.*, **6** [11], 1148 (1923).

[2] R. M. Howe and R. F. Ferguson, "A Study of Spalling," *Jour. Amer. Ceram. Soc.*, **4** [1], 32 (1921).

The slabs were a decided improvement. They were harder—had a clearer ring and gave much better service than the original mixture, but they were found to be a little too refractory with the result that the following mixture was tried:

30 grog
15 clay of low plasticity
55 bond clays
100

The grog in this mixture was selected for size as above. The mixture was prepared in the same manner as were also the slabs.

The results obtained have been very satisfactory. They seem to have the requisite characteristics enumerated at the beginning of this article.

In conclusion, the writer wishes to thank R. L. Clare of the Federal Terra Cotta Company for his interest in checking up the performance of these mixtures under their service conditions. Without this assistance very little progress could have been made.

M. D. VALENTINE & BRO. CO.
WOODBRIDGE, N. J.

Discussion

MR. PLUSCH: Our problem in slabs for grinding wheels is a very much more difficult problem than for terra cotta. The wheels weigh much more than terra cotta. They are solid and the abrasive has a specific gravity of nearly four. Our losses in slabs are much greater. We lose ware on account of defective slabs and these losses are considerably greater than in terra cotta because the value of our raw material alone runs around twelve cents per pound. So you can see that slabs which fail with us are a very serious proposition.

I have jotted down a few notes to stimulate thought regarding the manufacture of better slabs. Do we start right in the manufacture of slabs? Do we not pile our clays around in promiscuous places, wherever there is a convenient spot? Do we see that they are clearly marked? Do we test each car and follow it up as closely as we do the raw materials which enter into our product? I believe very few of us give anywhere near as much attention to the raw materials that enter into our slabs as we do the inspection and technical control of the product which we are manufacturing, whereas the very foundation of the material which we are making consists of the slabs on which the material rests while it is being fixed by heat. Do our mixture cards go out to the slab department in good, clear, concise form? Or, does some fellow measure with a wheelbarrow and make marks on the wall or some convenient board showing in a very crude manner what has been weighed?

Undoubtedly most of us know what size grog should be used, know that we should eliminate the fines and know that certain clays will not make good refractory slabs. After we have once determined what clays to use and what amount of each kind of clay to use, what size and amount of grog, how few of us consistently follow up succeeding batches to see that they are correctly proportioned, soaked and pugged? Slab mixtures are pretty generally slighted in most plants, and this is the main point that I wish to bring out.

Granted that we do inspect our clays carefully, proportion them carefully and accurately, that we use the proper grog, that we pug our clay correctly, do we fall down in the next step, namely, put the poorest laborer we can find around the place to making slabs? This is often the procedure in many plants and it seems to me to be the one place of all places where a good man should be put and kept, not changed around, and that the manufacture of slabs should not be left to any "green-horn" that is hired.

I do not think the clays we use play as important a part as the manner in which we use them. Just select good refractory clays, plastic and non-plastic, free from sand, good clean grog, free from fines, and you have the basis of as good a clay slab as can be made. The most important thing in the mixture, of course, is the skeleton or grog which is used, but here again comes the chance of slighting the mixture, once a proper mix has been determined. Maybe we have not time to size the grog properly, and we just rush ahead. Soon rush methods become standard, they are changed by the fellow who keeps the record in his hip pocket, instead of being directed to the laboratory, and losses keep creeping in.

Again I want to make a plea for more definite control of slab mixtures, from clay to the grog, through the preparation, through the pressing, through the drying, setting and firing. Take the firing for instance: it has been my experience in many places that slab kilns can be lighted and fired most any way, as long as they are fired slightly higher than the ware, under which they are to be used. No particular records are kept on the firing of the slab kilns, no predetermined charts laid out, no definite height determined as the best height for setting to prevent warpage or straining in firing. And here we ruin what might otherwise have been a good product. A good, common sense follow up of standard methods, but followed up continuously and religiously, will result in less slab losses and better slabs.

Firing records on experimental mixtures should not be left to someone who draws or sets kilns, but should be followed specifically by someone who has a knowledge of what he is doing. Too often good mixtures are started through and lost by some one fellow who has forgotten to keep track of them.

There are, of course, many problems which have not been settled regarding the best mixture, the best amount of grog, etc., but of course these conditions will vary for each plant and each different industry, and are problems on which coöperative research is often a value, but in which independent plant research is of the most value.

It is a question whether or not clay is the proper material from which to make slabs. A great deal of work has been done lately using silicon carbide in slabs. These should give an excellent account of themselves on account of their greater heat conductivity and their low coefficients of expansion. Of course, their price is initially very high and they would have to give many firings to be economical. Thinner bats may also be permissible in this material, thus effecting still greater economies. Mica schists have been suggested as refractories and some little work has been done on them in slab mixtures but has not been advanced far enough to get definite data.

There are many problems of a technical research nature that suggest themselves to me, but I am avoiding them at this time in making a plea for close follow-up on methods to see that they are carried out as outlined and consistently duplicated. This, to my mind, will be one of the biggest factors in producing better terra cotta kiln slabs.

I take this opportunity to ask any of the members of this Division to call at any time to see our plant at Philadelphia and to see our method of making and using slabs, which in our particular industry, are generally termed bats.

MR. BEECHER: It is worth while to emphasize the point which Mr. Plusch has just made, that control of mixtures and processes in the manufacture of slabs is usually slighted. The principal attention is given to the product of the factory and the manufacture of this essential piece of equipment is given but little thought until losses become very serious. Then when improvements are made or defects corrected the slabs are again forgotten until a similar story is repeated.

The use of very fine grog should be avoided. It produces a structure that cracks more readily upon heating and cooling in spite of the fact that it is much stronger mechanically. To keep the content of fines reasonably constant, it is necessary to keep close watch of the materials. When broken slabs are ground for grog in a dry pan for example, wet slabs will produce more fines than dry. Also when repairs are made to the machine, such as the replacement of plates or scrapers, there may be very marked differences in the fineness of the resulting grog. It is advisable, whenever possible, to screen the grog and use only a specific size or mixture of sizes. In this way variations due to the conditions of the machine and of the material ground can be avoided.

Slabs made by machine pressing are commonly inferior to those hand made. This is probably due to the cracks formed in the crumb during pressing. These cracks collect oil from the surfaces of the mold and when the sides are forced together again at the end of the stroke the oil prevents the healing of the crack. This mechanism can be readily observed if the plunger is withdrawn at different stages of deformation of the crumb and the development and subsequent closing of the cracks observed.

Unfortunately it is not possible as yet to state definitely what economies would result from the use of silicon carbide slabs in the terra cotta field. They have been used for some time in the manufacture of grinding wheels and records of 40 to 50 firings per slab have been reached but the slabs are still in use so the total life to be expected is not known. Under similar conditions normally good fire clay slabs give five to six firings.

E. C. HILL: Our slab loss is about 3 or 4% which means that our slabs will stand twenty-five or thirty firings. In firing with coal, the temperature change is not so great as with oil, and as a result, our slabs stand up better.

ON THE STRENGTH OF HEAVY CLAY PRODUCTS

By J. H. Griffith[1]

ABSTRACT

The published strengths of standard clay products have been formulated in simple equations (1) for placing the information in a simple compass for architects and ceramists, (2) to show the law of variation in terms of properly chosen variables, (3) to aid in appropriate selection of variables in devising future tests. The author assumed that a plus or minus variation or "tolerance" of 10% from the averages found by tests would be acceptable to manufacturers and ceramic engineers and has endeavored to keep well within these limits.

Introduction

It is the purpose in this paper to discuss simple laws for defining the strengths of heavy clay products. It is assumed to this end that the practical needs of ceramists and engineers will be subserved if these strengths are determined so that the probable errors shall not exceed five or ten percentages of the averages found by tests. It will be shown that this can be done with a little statistical correlation and proper choice of variables.

Building Brick

The researches of Howard, Bragg, and others suggest the compression strength of a brick is a function of the type of clay, the method of manufacture, its density and degree of firing in kiln, the modulus of rupture of the brick, etc. The writer is of the opinion that the most opportune choice of a single independent variable would be the "absorption." The degree of firing and density have already been correlated by Orton[2] with the absorption percentage. Recent information conveyed to the author by Paul Cox, Head of the Ceramics School of Iowa State College, leads him to expect that absorption connotes to some extent geographical location. The absorption test is very simple requiring a minimum of apparatus, little technical skill, with attention only to getting initial and final weights.

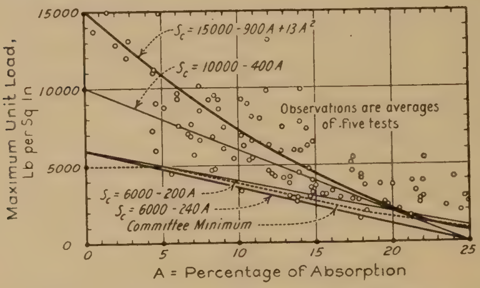

Fig. 1.—Compression strength of American brick.

A plot of the data collected by the Committee C-3 of the American Society for Testing Materials on American building brick shows that the compression strength for all practical purposes is a decreasing function of the absorption. A fairly representative portion of this data has been compiled in a convenient compass by Professor Withey.[1] This is plotted in Fig. 1, each observation being a mean of five tests. The simple law, $S_c = 15{,}000 - 900A + 13A^2$ gives the average compression strength of an American brick in terms of the absorption, A, and in practical conformity with the statistical treatment of the theory of Least Squares In other words the sums of the squares of the deviations (residuals) or the moments of the approximate errors are taken small. The figures have been selected to give satisfactory constants for practical computation.

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[1] Prof. of Experimental Engineering, Iowa State College, Ames, Iowa.

[2] *Proc. A. S. T. M.*, **15,** 263.

An equation $S_c = 10{,}000 - 400A$, still simpler for mental calculation, may be found by taking the approximate trace of the lower range of probable error deviation. In other words it is much better than an even wager that the compression strength of an American brick will exceed the value given by this equation. Brick with absorptions greater than 25% are automatically eliminated. There are few such.

The equations $S_c = 6000 - 240A$ or $S_c = 6000 - 200A$ are still more conservative and fully as simple for mental calculation. They meet moreover the spirit of the rulings of the Committee if not the exact letter. The strengths automatically vanish for absorptions exceeding 25 and 30%, respectively.

Brick Piers

The tests of large brick piers conducted by Bragg[2] under the advisory direction of Orton and Bleininger are still being discussed by the members of this SOCIETY. One may, however, disregard, in the writer's experience such subtilities as "grades," "bonds," "courses," and even the ages of the mortars of the test specimens, in favor of the fundamental variable—as before, the absorption. The author has found after a number of trials and modifications that the following equation meets the analytic function of strength very satisfactorily within the domains imposed:

$Sp = mg[3800 - 300A + 6^1/_2A^2]$
Sp = compression strength, pounds per square inch
A = percentage of absorption
m = 1 for cement and cement-lime mortars (1:3)
= $^1/_2$ for lime mortars (1:6)
= $^1/_4$ for lime mortars (1:3)
g = 2.8 for New Orleans District
= 2.2 for New York District
= 1.2 for Chicago District
= 1.0 for Pittsburgh District.

The subsidiary variables mentioned previously have no pronounced bearing on the strength as far as statistics show. The salient strength functions have been calculated and recorded in Table I for comparison with the averages of the tests. The reader may calculate the average deviation close enough mentally from the table and easily form his own inductions as to the probable error when employing the equation.

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[1] Johnson's "Materials of Constructions," 5th Ed., pp. 282–3.

[2] Bur. Stand., *Tech. Paper* **111** (1918).

Hollow Tile Walls

The rule employed in cement proportioning suggests itself in dealing with hollow tile walls. In other words one might say the strength is a direct function of an independent variable connoting,—say modulus of rupture, degree of firing in kiln, tensile strength, etc., and is an inverse function of voids, absorption percentage, or unity minus density. Contrariwise since Orton has correlated the relative vitrification with absorption and Hathcock has shown the strength of tile individuals is a decreasing function of this variable, the absorption would appear again to be the essential conditioning variable. In view of the fact that "run of kiln" is apt to be chosen in building construction resulting in a chaotic distribution as regards absorption factors, it would seem wise to select another variable. A study of Whittemore and Hathcock's recent paper[1] indicates that the gross area per lineal foot of wall measured transversely is a variable that will best appeal to both architects and builders in a simple equation of the form $S_t = K[cA_g + N]$. As an illustration, taking the Ohio tile of this investigation having the "cells" vertical the strength per running foot of length of wall is $S_t = 15[8A_g + 1]$ with the strengths of tile for the cell axes running horizontal about 0.4 as much or $S_t = 6[8A_g + 1]$. The data for the New Jersey lot of tile are too meager for precise inductions. The walls in this research were constructed to realize the maximum efficiency of the product rather than commercial practice. The strengths estimated by equations should be modified by architects to conform with practice.

Drain Tile

While the strength of drain tile is conditioned by the absorption and other minor variables it is clear the rated diameter is the major independent variable. The equation $S_D = K\left[1050 + 10D + \frac{2D^2}{3}\right]$ appears to meet all the analytic needs of a practical formula conforming to the ruling of the Committee of the A. S. T. M.[2] quite closely considering the simple computing parameters involved. Table II shows the concordance of the equation with the published strengths using parameters $K = 0.7$ for farm tile, $K = 1.0$ for standard drain tile, and $K = 1.4$ for extra quality drain tile.

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[1] Bur. Stand., *Tech. Paper* **238,** 525 (1923).

[2] Stand. Specif. A. S. T. M. for 1916.

TABLE I

STRENGTH OF LARGE BRICK PIERS BY TESTS AND BY FORMULA. $Sp = mg[3800 - 300A + 6^1/_2A^2]$

Sp = compression strength, lbs./in.^{2} A = absorption percentage m = mortar g = location factor

District	Pittsburgh						Chicago		New York		New Orleans	
	$g = 1.0$						$g = 1.2$		$g = 2.2$		$g = 2.8$	
Absorption A	Cement or Cement-Lime Mortar $m = 1$		Lime Mortar 1:6 $m = ^1/_2$		Lime Mortar 1:3 $m = ^1/_4$		Cement-Lime Mortar 1:3 $m = 1$		Cement-Lime Mortar 1:3 $m = 1$		Cement-Lime Mortar 1:3 $m = 1$	
	Formula	Test	Formula	Test	Formula	Test	Formula	Test	Formula	Test	Formula	Test
Percentage	lbs./in.^{2}											
1.28	3427	3800, 3220, 3300 Av. 3440										
4.08	2684	2710, 2740, 2900 Av. 2783	1342	1450, 1270, 1360 Av. 1360								
7.46	1924	2000, 2070, 1760, 1760 Av. 1898	962	840, 890, 990 Av. 907								
15.16	746	870, 870, Av. 870										
16.20	646						775	840, 790, 810, 750, 700, 710 Av. 767				
16.28	639	510, 560, 650 Av. 573			160	210,178, 126 Av. 171						
16.40	628								1382	1170, 1300, 1260 Av. 1243	1758	1630, 1790 Av. 1710
16.80	595										1666	1450, 1760 Av. 1605
17.10	571										1599	1880, 1690, 1660 Av. 1743
18.60	470								1032	1280, 1280, 1220 Av. 1260		
19.30	431								948	1070, 1060, 1020 Av. 1050		

TABLE II.—STRENGTHS FOR DRAIN TILE OF COMMITTEE A. S. T. M. AND BY FORMULA

$$S_c = K\left[1050 + 10D + \frac{2D^2}{3}\right]$$

S_c = Average supporting strength in pounds per lineal foot

D = Internal diameter of tile. K = parameter as follows

Internal diameter, inches	Minimum supporting strengths per foot					
	Farm drain tile $K=0.7$		Stand. drain tile $K=1.0$		Extra quality drain tile $K=1.4$	
	Formula	Comm.	Formula	Comm.	Formula	Comm.
4	771	800	1102	1200	1543	1600
6	794	800	1134	1200	1588	1600
8	821	800	1173	1200	1642	1600
10	852	800	1217	1200	1704	1600
12	886	800	1266	1200	1772	1600
14	925	900	1321	1200	1849	1600
16	967	1000	1381	1300	1933	1600
18		——	1446	1400	2024	1800
20		Limit	1517	1500	2124	2000
22			1593	1600	2230	2200
24			1674	1700	2344	2400
26			1761	1800	2465	2600
28			1853	1900	2594	2800
30			1950	2000	2730	3000
32			2053	2100	2874	3200
34			2163	2200	3028	3400
36			2276	2300	3186	3600
38			2393	2400	3350	3800
40			2517	2500	3524	4000
42			2643	2600	3700	4200

Sewer Pipe

The same formula employed for drain tile applies to sewer pipes tested according to standards of A. S. T. M. on two point bearings and of diameters ranging from 4 to 42 inches if the parameter K has a sliding scale ranging 0.9 to 1.3 in the interval 4 to 42 $(0.9 < K < 1.2 : 4 < D < 42)$.

Conclusions

The conclusion is drawn that a rational theory for the strengths of the heavy clay products is easily possible of attainment. It will be partly dynamical and partly statistical. Such a theory should not be concerned with utilitarian motives alone as in the present case. Instead the laws of the various stress functions should be expressed as mathematical surfaces in terms of all the conditioning variables for analytical study and the scientific development of the subject. A theory of heavy clay products, including pavers, at the present time would greatly aid in formulation of a logical rationale for future testing practice and would reduce the uncertainties involved by extrapolation at the present time.

NOTE: The writer acknowledges the criticism and advice of Paul Cox and D. A. Moulton in the preparation of this paper.

NOTES ON TERRA COTTA BODY SHRINKAGE[1]

By P. G. Larkin and E. R. Curry

ABSTRACT

Notes on method of preparing a terra cotta body, proportioning by volume and using unground material, and method of preparing body, proportioning with ground materials, using disc feeders, are given. Notes on checking laboratory work with these two methods and variation in shrinkage due to amount of water in the body are also considered.

The problem of shrinkage control of the terra cotta body is a somewhat prosaic but very necessary task. These few notes are presented because of the points of general interest they may contain on this problem.

Until recently we have used the older method of proportioning a terra cotta body, using certain volumes of clay, coarse crushed grog, or other material. In the system now in use all materials are ground separately to pass a fine screen, and then proportioned with disc feeders.

These notes are the result of observations during the change from one process of body preparation to the other.

In the older method of preparation, there was little attempt to crush the lumps of clay. Any size which could pass through the bin outlet was used.

The grog had only undergone a preliminary crushing such as is accomplished by gyratory crushers.

The non-plastic clay referred to hereafter was fairly finely divided by the time it was placed in the bins.

The materials were fed from the bins into what was called a mixing car of about forty-five cubic feet capacity. There was an endeavor to get a certain height of each material in the car; the contents of the car were then dumped into a hopper and fed into a dry pan. The body was ground to pass 14-mesh.

A typical body composition by volume, using this method, follows:

$$\text{Per cent}\left\{\begin{array}{l}41.0 \text{ terra cotta clay}\\ 11.7 \text{ non-plastic clay}\end{array}\right.\qquad 47.3 \text{ grog}$$

In the new method of body preparation all the materials are ground separately in a dry pan to pass 14-mesh screen. They are then proportioned by means of disc feeders. The volume composition of a body having practically the same shrinkage as the one above was

$$\text{Per cent}\left\{\begin{array}{l}50.3 \text{ terra cotta clay}\\ 9.0 \text{ non-plastic clay}\end{array}\right.\qquad 40.7 \text{ grog}$$

The change in proportions of volumes of clay and grog in the two methods of preparation is due to a greater volume increase of the clay, which is in a much finer divided state than the grog. On the basis of weights of course both compositions must be the same.

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[1] Presented at the Summer Meeting, Los Angeles, Calif., Oct. 6, 1924.

In all laboratory work on bodies, materials have been ground separately, and then proportioned by volume. Using the same proportions as in the old mixing car system, we have not been able to check laboratory shrinkage results with the shrinkage results of the body prepared in a larger way. Our total shrinkage values in general have varied from 4.20% to 4.60%, in comparison with the average value of 6.66% in actual practice.

On the other hand when the proportions of the new system have been used in laboratory work, the shrinkage results have been very nearly the same as in actual practice. For example, the large shrinkage trials for a period had an average total shrinkage value of 6.91% and an average moisture content of 26.3%. At this time some laboratory trial pieces which were made had an average total shrinkage of 6.83% and a water content of 26.3%.

Therefore when the bulk method of proportioning is used, laboratory shrinkage results may be made to check fairly closely with actual practice, by finding the volume changes which occur with the constituents in reducing them from coarse to finely ground materials, and making corrections in the composition accordingly.

Effect of Water on Shrinkage

In attempting to discover the causes of variation in shrinkage, the effect of variable amounts of water has been noted. An average figure for water content for our terra cotta body is 26%, based on dry weights. The body mixture on this basis has a total linear shrinkage of 6.8%, fired at cone 4. In checking the per cent moisture in the body, samples have been taken from the same wads of terra cotta body used for pressing shrinkage trial pieces, and at the time they were pressed. A variation of from 25.2% to 29.0% water content has been noted in one day, and the total shrinkage of the two trial pieces was 6.07% and 7.04% respectively.

In order to be sure that such variation was not largely due to variation in the character of the clay, we have taken dry terra cotta body, mixed it thoroughly, and tempered with different percentages of water. In one such experiment with water contents 24.5% and 27.0% there resulted total shrinkages of 5.82% and 6.66% respectively fired at cone 4. At another time with 22.1% and 27.5% of water there was a total shrinkage variation of from 5.21% to 7.02% respectively, fired at the same temperature. These values were the average of eight 1″ x 1″ x 8″ shrinkage bars.

There is some variation due to the character of the clay, but the data indicate that if an accurate method of control of water content could be devised, our shrinkage problems would be measurably simplified.

Gladding, McBean and Co.
Lincoln, Calif.

THE USE OF RADIATION PYROMETERS ON REFRACTORY KILNS[1]

BY CHARLES B. THWING

ABSTRACT

The high cost of maintenance of platinum thermocouples has greatly discouraged the use of pyrometers on kilns firing silica and other high refractories.

The method of using a combination recorder employing thermocouples for the lower ranges of temperatures and the radiation pyrometer for the higher ranges is described.

The accuracy of the measurements is fully equal to those made with platinum thermocouples at a temperature for which the latter are durable, and the radiation pyrometer has the advantage of not deteriorating at high temperatures.

Neither couple nor radiation tube is damaged by removal while hot, so that the tubes may be kept in constant service, thus making the cost of the complete installation very reasonable.

The high cost of maintenance of platinum thermocouples has greatly discouraged the use of pyrometers on kilns firing silica and other high refractories.

About six years ago, at the request of O. M. Reif, Vice-President and General Manager of the Harbison-Walker Refractories Company, G. K. Slotterer, Superintendent of the Chester and Downingtown Plants of that Company sought the advice of the writer concerning the possibility of obtaining an efficient and economical pyrometer equipment for their silica kilns.

We worked out together the plan which was tested out for four years at the Downingtown plant.

The results obtained were so satisfactory that in 1923 the Company ordered at one time similar equipment for six additional plants covering ninety kilns.

The General Refractories Company also has ordered equipment of the same sort for one of its plants.

The radiation pyrometer is the same, with some improvements, as we have been using since 1908 on lime and cement plants and glass plants. It is not sensitive for low temperatures.

In order to cover all parts of the temperature scale from water smoking to finish with a chart having an open scale a two galvanometer recorder is used. One galvanometer records temperatures up to 1600° from a base metal thermocouple; the other records high temperatures from the radiation receiving tube.

Each galvanometer records two kilns, the records being distinguished by dash and dot. Each recorder is at one time recording two low and two high kilns.

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[1] This paper is preprinted for use at the Annual Meeting of the AMERICAN CERAMIC SOCIETY, Columbus, Ohio, February, 1925, and does not constitute a release to the press.

The mounting is designed primarily for the radiation tube but serves equally well for the thermocouple. It consists of a square refractory hollow block having an inside diameter of about 7 inches. The closed end of this muffle, which projects a few inches through the crown of the kiln is ground to a uniform thickness of $1^1/_2$ inches.

The top of the muffle is closed by a flanged cover having a circular hole through which the couple is inserted. When the recorder shows a temperature of over 1600° the thermocouple is disconnected and removed and the radiation tube put in position above the hole and connected to the same wires formerly used for the couple.

At the same time the necessary changes in the recorder connections are made at the plug switchboard in the pyrometer room.

The pyrometer mounting on the kiln is protected from the weather by our usual ventilated brick housing which also serves to smooth out the larger variations in the temperature.

When desired the block may be installed through the side wall, or the block may under some conditions be omitted and the tube pointed directly at the ware.

When the last mentioned plan is adopted it is well to provide a vertical blast of air in front of the opening to screen the instrument from occasional outrushing flames.

The accuracy of the measurements is fully equal to those made with platinum thermocouples at the temperatures for which the latter are durable. The radiation pyrometer has no upper limit of temperature. We have successfully measured temperatures above 4000°F in a tungsten furnace. The higher the temperatures the more efficiently the pyrometer functions.

Barring accidental breakage of the muffle, which can with care be forestalled, the radiation tube is not subject to damage and the interior of the tube is so sealed in that the calibration remains constant for a long period of time.

Neither couple nor radiation tube is damaged by removal while hot, so that the tubes may be kept in constant service, thus making the cost of the complete installation very reasonable.

President, Thwing Instrument Co.
Philadelphia, Pa.

A MICROSCOPIC STUDY OF STRESSES IN GLAZES[1]

By Arthur V. Henry

ABSTRACT

Stresses in glazes are studied making use of the microscopic method. The investigation indicates that differential coefficient of expansion is partially responsible for stresses in glazes.

There are several possible explanations which may account for stresses in glazes.

1. Seger in his "Collective Writings" attributes stresses ordinarily to the differential coefficient of expansion between the body and the glaze.
2. Since a glaze is not a homogeneous substance, there will be a differential coefficient of expansion between the various sections of the glaze itself.
3. A glaze in cooling tends to crystallize. A change in volume accompanies crystallization, bringing about stresses.
4. New compounds may form after the glaze has become rigid and introduce stress.

The following work was done in an effort to determine how much of the stress in a glaze was due to the differential coefficients of expansion between the body and glaze.

Theory

A glass is an amorphous substance and normally isotropic, *i. e.*, it will transmit light with equal velocity in all directions. If, however, the glass is subjected to a stress, it becomes anisotropic and a ray of light passing through it, will be broken up into two rays of unequal velocity. The difference in velocity of these two rays becomes greater as the stress increases. It has been proved[2] that the stress in a glass is directly proportional to the birefringence or difference between the indices of refraction of the two rays.

The index of refraction of a substance is the inverse proportion of the velocity of light through the substance to the velocity of light through air, the latter being taken as one. The birefringence multiplied by the length is called the optical path difference, which quantity can be measured by means of a microscope and a compensated quartz wedge. The optical path difference $(n_a - n_b)l$, divided by the length of path is obviously the birefringence of the glass under test $(n_a - n_b)l$, where n_a = index of refraction of one ray, n_b the index of refraction of the other, and

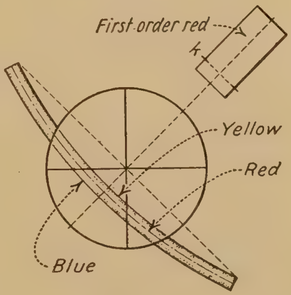

Fig. *A*.

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[1] Recd. Jan. 13, 1925.

[2] L. H. Adams and E. D. Williamson, "The Relation between Birefringence and Stress in Various Types of Glass," *Jour. Wash. Acad. Sci.*, 9 [20], Dec. 4 (1919).

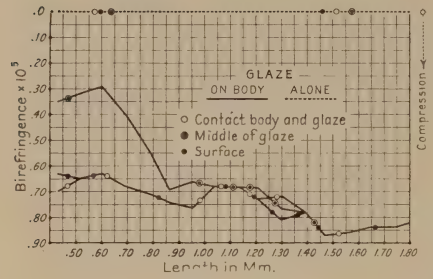

FIG. 1.

l the path length. The following curves represent a variation of birefringence or stress multiplied by a constant, throughout the length of the glaze.

A simple experiment can be made showing the effect of stress upon glass. If a narrow (one-half inch) strip of ordinary window glass is placed under a microscope at the 45° position between crossed nicols and bent slightly with the fingers the following reactions will take place when viewed through a selenite plate. The edge of the plate under tension will become blue; the center or neutral zone, red; and the edge under compression, yellow.

This theory was applied to the work on glazes.

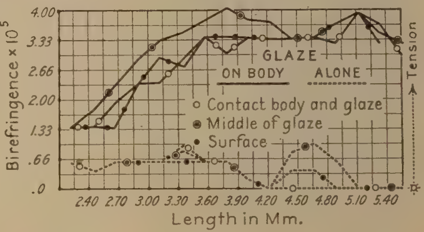

FIG. 2.

Method

A section of body and glaze was removed from tile, cemented to the end of a rotating stage and immersed in oil. The whole was then placed under the microscope between crossed nicols and the optical path difference of the ray of light passing through the length of glaze was read off on a compensated quartz wedge. The wedge was graduated in 10 *yy* divisions and could be read with an accuracy of one division. Readings were taken at intervals along the glaze. The glazed test piece was then cemented to a glass plate with Canada balsam and the body ground off using emery powder and water. Similar readings at the same intervals were made and curves drawn. The extreme thinness of the glaze in Fig. 1 necessitated the use of a 16-mm. objective. A 32-mm. objective was used with the remaining glazes.

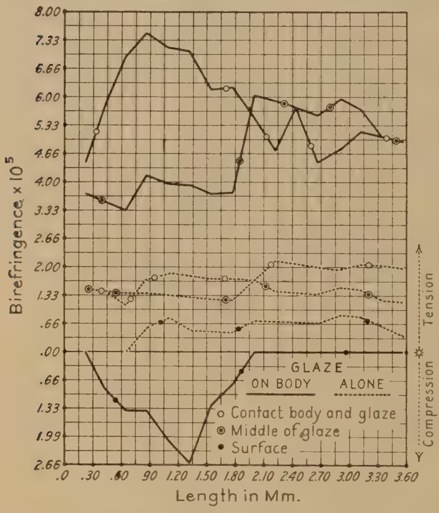

FIG. 3.

Figure 1 represents a commercial

glazed tile that showed no tendency to craze or shiver. The glaze is under a fairly uniform compression throughout. No stress was detected in the glaze after the body was removed.

Figures 2 to 9 represent tile glazed in the laboratory. All crazed badly. The glaze of Fig. 2 has the formula:

$$\left.\begin{array}{l}0.15\ K_2O\\0.15\ Na_2O\\0.40\ CaO\\0.30\ PbO\end{array}\right\}\begin{array}{l}0.20\ Al_2O_3\\1.0\ SO_2\\0.333\ B_2O_3\end{array}$$

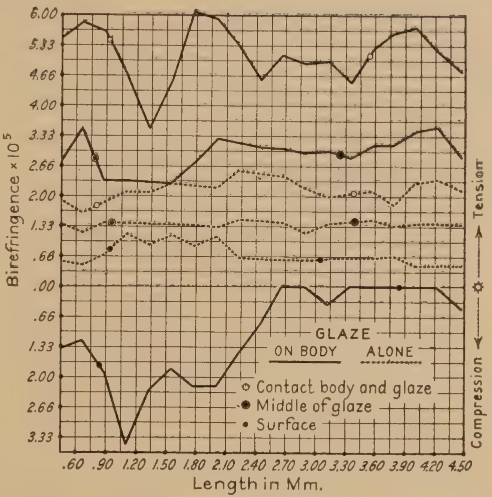

FIG. 4.

and was fired to cone 5. On the curve, it is seen to be under considerable tension, somewhat greater in the middle of the glaze than either at the contact between the body and glaze or at the surface. The glaze alone shows slight tension.

Figure 3 represents a glaze of the formula

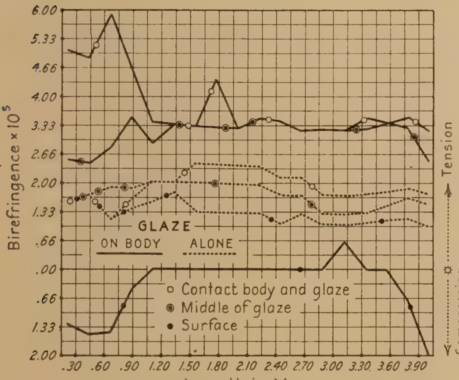

FIG. 5.

$$\left.\begin{array}{l}0.15\ K_2O\\0.15\ Na_2O\\0.40\ CaO\\0.30\ PbO\end{array}\right\}\begin{array}{l}0.20\ Al_2O_3\\1.33\ SiO_2\\0.44\ B_2O_3\end{array}$$

fired to cone 05. The dividing surface between the body and glaze and the middle of the glaze shows a high degree of tension while the surface is under rather high compression. With the body removed the glaze shows a uniformly low tension.

Figure 4 is a test of another section of the same tile as Fig. 3, giving similar results.

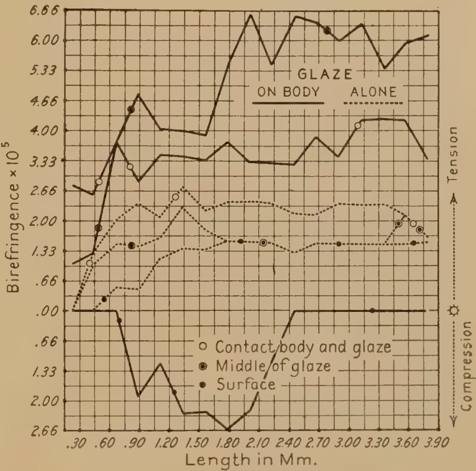

FIG. 6.

The formula of the glaze in Fig. 5 is

$$\left.\begin{array}{l}0.15\ K_2O\\ 0.15\ Na_2O\\ 0.40\ CaO\\ 0.30\ PbO\end{array}\right\}\ 0.20\ Al_2O_3\quad 1.5\ SiO_2\quad 0.5\ B_2O_3$$

It was fired to cone 05.

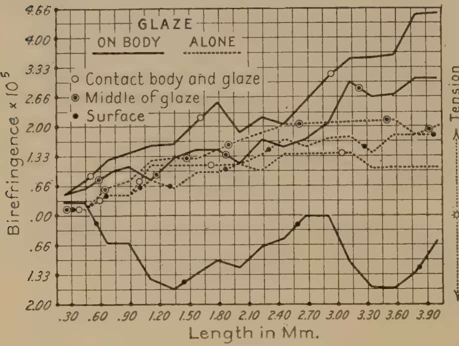

FIG. 7.

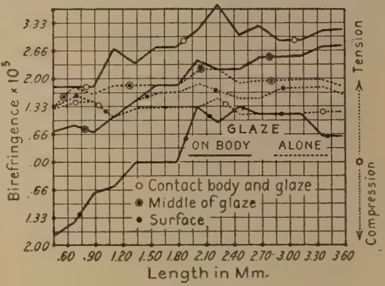

FIG. 8.

Figure 6 represents another section of the same tile as in Fig. 5.

Figures 7 and 8 are tests on glazed tile of same composition as those of Figs. 5 and 6 but fired at cone 1. These show less stress probably due to greater solution.

Figures 5*a*, 6*a*, 7*a* and 9 show how the stress varies from the point of contact with the body to the surface of the glaze. In the first three of the figures named, the stress (tension) increases approximately up to one-third of the thickness of the glaze and then decreases through a neutral zone of zero stress to a decided compression, except in Fig. 9. The fact that the stress is less at the point of contact than at one-third the thickness of the glaze, is probably due to the partial solution of the body by the glaze.

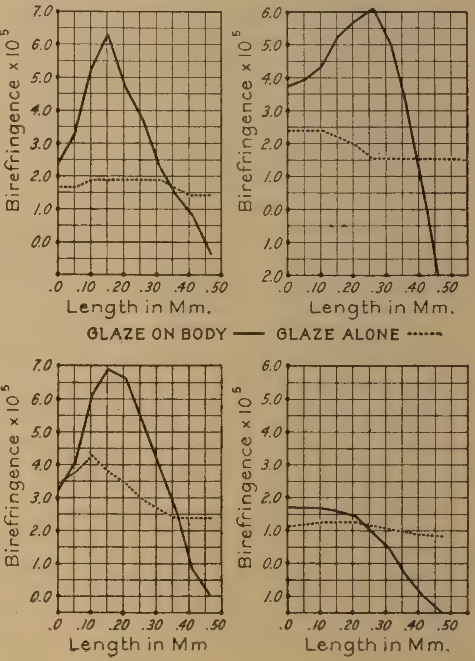

FIG. 5*a*, 6*a*, 7*a*, and 9.

Conclusions

The differential coefficient of expansion between the body and glaze is an important factor in causing stresses in glazes. Stresses are introduced to a less degree through other causes. It appears desirable to have a glaze under slight compression at room temperatures. Acknowledgment is made for the assistance and suggestions of Dr. Wm. McCaughey.

Ceramics Department
Ohio State University

MANUFACTURE OF REFRACTORIES BY DRY PRESS METHOD[1]

By Earl Hagar

ABSTRACT

A brief description of the manufacture of refractories by the dry press method is given emphasizing the following points in the preparation of materials: (*a*) weathering, (*b*) grinding and tempering, (*c*) screening, (*d*) mixing; the pressing of shapes and the amount of pressure is described. Six points are given as advantages of the dry press method, chief of which are reduction in cost of manufacture and increase of life of ware.

Both the manufacturers and users of fire brick and shapes are benefited by refractories made by the dry press method. Among numerous advantages, the cost of manufacture is greatly reduced, and the life of the ware is greatly increased.

Since the dry press process is comparatively a recent development, and some manufacturers are not yet familiar with its distinct advantages, the development and extension of the dry press method calls for an explanation of the special requirements and resulting advantages of its use.

The successful manufacturing of magnesite and chrome brick, and fire clay brick from non-plastic flint clays is evidence that it is both possible and practical to manufacture refractory shapes by the dry press method.

Preparation of Materials Important

Weathering

It is not the kind of materials used, but the method of preparation and pressing that brings results. Although a high percentage of plasticity is not essential for dry press ware, the best brick is produced with the least expense, trouble and loss when the plasticity of the raw material is developed. This should be done by weathering the raw material in storage piles, or by storing the freshly ground clay in a moist condition. In general, the clay should weather not less than forty-eight hours, but a greater length of time will be an advantage.

Grinding and Tempering

In grinding the material, any method may be used that will produce the fineness required. If by a dry pan the final amount of moisture may be admitted at the pan on the theory that if the full percentage of moisture is contained at this point, the grinding operation will have some of the beneficial effects of a wet pan and develop the full plasticity of the clay. However, any other method of mixing the water with the clay may be used that will distribute evenly the fine and coarse particles without causing the clay to form small, damp balls. These damp balls are detrimental to the mechanical operation of the press, and cause the product to be of a coarse nature. A common test to determine the proper condition of the material is to squeeze some of the material in the hand. If it balls up and stays

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[1] Recd. Dec., 1924.

in a compact shape, and breaks without being shattered, it is in proper condition for the dry press. If, however, this hand pressure squeezes water out of the clay, it contains too much moisture, but in general, the higher the percentage of moisture without any excess, the better the ware. A mixture too dry produces poor corners and edges and when fired is usually soft and shells easily.

Screening The clay which goes through the pan or other grinder should pass through some type of screen. Although the percentage of coarse sizes in various clays is variable, it is very important that the percentage of finely ground clay be sufficient to fill the voids between the coarse particles. If the percentage of coarse particles is too large, the plasticity of the entire mass is greatly reduced even though the clay be classed as highly plastic. The grind or size of screen used must be determined from the clay used, to satisfy the needs of the consumer. In general, the fine grind works the better in the press and makes a stronger, denser and better appearing brick.

Mixing It is very essential that some form of mechanical mixer should be used just above the press to keep fine and coarse particles evenly mixed, being fed into the press through a perpendicular chute. A chute built at an angle will cause the coarse particles to run ahead of the finer ones, thereby destroying the uniform mixture. It is very important that an even, uniform mixture be maintained at all times if the best results are to be obtained. Whenever the moisture content changes, the amount of material and strength of bond in the product changes.

It is important, too, that the material used in the manufacture of large refractory shapes by the dry press method be uniform and homogeneous. Without this uniformity and homogeneity one may encounter serious difficulties in the manufacture of large shapes. The shapes would have an undue tendency to check or crack while drying, and it would also cause warping and cracking while firing. However, with proper care one should make shapes as large as 24 x 12 x 4 inches, or even larger without any serious difficulty.

Pressing of Shapes

There are a large number of shapes being used today that are practical sizes to be made by the dry press process; also various 9-inch sizes. To equip the press for making these properly is very important. One should have even distribution of material in the mold box according to the shape of the brick. For example, if it is a standard 9-inch No. 1 wedge, the mold must contain more clay at the thick end. This can be done successfully by means of a tapering device attached to the charging box that will cause the clay to be left in a tapered pile on the mold box. The same principle may be applied to arch brick, and all other difficult shapes.

The Amount of Pressure

The amount of pressure is important since upon pressure greatly depends the results of dry press brick making. This pressure at times equals five to six thousand pounds per square inch. The amount of pressure depends upon the class of the clay, and the amount of moisture. In some cases high plasticity will cause the ware to split or "pressure crack." The addition of grog or calcined material assists in overcoming this trouble. Dry pressing should be done under the highest pressure possible. High pressure causes the ware to split, but this trouble can be reduced by increasing the period of pressure. This may be done by cutting down the speed of the press, or it may be built in the machine mechanically. In general the greatest possible pressure produces the best brick.

Advantages of Dry Pressing

Some of the advantages to be gained by making brick and large shapes by dry press process are:

1. The cost of manufacture will be reduced.
2. The cost of installing expensive driers or dry floors will be lessened since standard sized brick and most shapes are sometimes set direct from the machine to the kiln.
3. The resultant ware will be more uniform and exact in size, which is very important in construction of furnaces.
4. The refractoriness of some clays will be increased.
5. The uniform size of ware will reduce the fire clay used in the joints.
6. Large refractory shapes, made by the dry press process are able to withstand sudden changes of temperature much better than shapes made by any other process.

Therefore, refractory manufacturers and refractory users should investigate thoroughly the use of fire brick and large shapes made by the dry press method, thereby reducing cost of production, and in turn giving their customers the very best service possible.

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Vol. 8 **March, 1925** **No. 3**

ORIGINAL PAPERS

LIMESTONE FOR SHEET GLASS MAKING[1]

BY EDWIN P. ARTHUR

ABSTRACT

Quarry selection is suggested as a more rational basis for the specification of a limestone for making sheet glass than limits of chemical composition. Non-representative sampling is recommended in testing limestone for contamination.

The proper quality of lime and limestone for glass making has been the subject of some discussion[2] but sufficient emphasis has perhaps not been placed on the requirements of a limestone for sheet glass and window glass manufacture. Sheet glass, including all glass drawn from the molten melt,[3] must be of the very highest quality to meet the present demands of the market.[4] With the exception of optical glass and some specialties, it seems probable that drawn sheet glass requires higher quality raw materials and more careful process control than any other glass. This is true not only because of the large unit sizes of the ware[5] and the purposes for which sheet glass is used, but also because of the peculiar nature of the process of manufacture. The "drawing operation" very materially exaggerates the size of any seeds or stones in the glass and makes more conspicuous any slight defects in the body of the glass. Maintaining the color of a flint glass tank subject to heavy load requires a similar careful control of furnace conditions and temperatures.[1]

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[1] Recd. Jan. 21, 1925. Presented at the Annual Meeting of the AMERICAN CERAMIC SOCIETY, Columbus, Ohio, Feb., 1925. (Glass Division.)

[2] Turner, English, and others, *Jour. Soc. Glass Tech.* U. S. Bur. Stand., *Bull.* **118,** "Tentative Specification of Limestone for Glass Making," Peddle, "Glass," **1,** 148 (1924), and many others.

[3] The latest methods of making plate glass involve a drawing operation.

[4] "Master Specification of Glass for Glazing," U. S. Bur. Stand., *Circ.* **164.**

[5] A sheet of window glass 40″ x 60″ weighs about 26 pounds.

Of the raw materials used for sheet glass making, limestone is most subject to variation.[2] The alkali furnished to the trade is manufactured under strict technical control. The preparation of glass sand is a well-developed industry. Limestone, on the other hand, is largely supplied from stone quarries where the main production centers on furnace flux, building material or burned lime rather than a special product for the glass trade.

Limestone deposits are generally worked with high explosives from a vertical face into the quarry opening the depth of which is determined by the water level and the character of the deposit. Overburden is removed either by hand or with power scrapers. Frequently, if the overburden is very light, no attempt is made to remove it. A rough selection of stone is often made in quarries where quarry cars are loaded by hand, but selection is impractical where loading is done with power shovels. In some districts, the tendency has been in recent years to abandon open quarries and operate underground stone "mines." Mining avoids certain overburden troubles

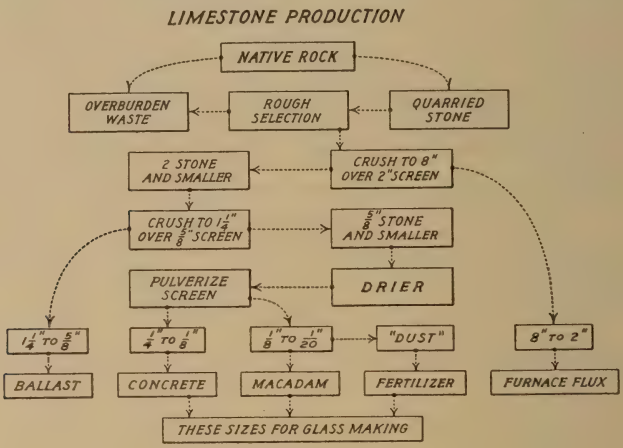

FIG. 1.

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[1] Window glass is sensitive to oxidizing or reducing conditions in the furnace, somewhat less sensitive, however, than colored or flint glass.

[2] In this connection it would be well to note that the iron content of ordinary window glass is not considered important. Any amount of iron less than 0.25% Fe_2O_3 is considered satisfactory by the present demand of the market.

and permits a very flexible operation independent of weather conditions.[1] Resort has also been made to washing in an effort to eliminate contamination from overburden and mud seams as well as limestone dust.[2] A typical quarry operation is shown in Fig. 1.

The relative amounts of different sizes of stone produced depend somewhat on the character of the native rock. The preparation of the larger sizes always leaves some "fines" for which the quarryman is often glad to find a market. It is apparent from the diagram that any quarry debris from overburden or mud seams will pass through the milling with the fine ground stone. Subsequent screening of the pulverized stone will leave most of the dirt in the last separation. This fact offers a logical explanation to the belief of many glass makers that "fine ground limestone makes stones in glass." Fine ground limestone as a general rule, is more subject to contamination than are the larger sizes.

Just how serious quarry contamination may become is shown by the two tables of analyses of car-lot representative samples from a quarry in the Shenandoah district. Table I apparently indicates a uniform stone of fair quality. It is certain that this stone could not be condemned for glass making on the basis of the chemical analysis. In reality, however, this stone was uniformly contaminated with overburden debris. A very inferior glass was made from this limestone. An investigation of the quarry operation showed that the finished stone contained practically all the foreign matter loaded from the quarry.[3] A rigid selection system in the quarry made possible the production of a much better stone as reflected

I—QUARRY RUN

Sample	SiO_2	R_2O_3	$CaCO_3$	$MgCO_3$
16217	2.13	0.48	95.37	1.46
16307	2.15	0.38	94.78	1.52
16311	2.24	1.01	94.62	1.65
16325	2.42	1.24	95.29	1.40
16506	2.69	1.66	95.06	0.98
16508	2.36	1.02	95.96	1.14

II—SELECTED STONE

Sample	SiO_2	R_2O_3	$CaCO_3$	$MgCO_3$
41219	0.66	0.70	97.44	1.08
41220	0.40	0.48	97.44	1.34
41221	0.52	0.52	97.46	1.22
41222	0.64	0.64	97.69	0.84
41224	0.82	0.56	97.13	1.02
41226	0.86	0.64	97.24	0.94

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[1] See paper presented by J. R. Thoenen on limestone production as a mining problem before American Institute of Mining and Metallurgical Engineers, Feb., 1925.

[2] Michigan Limestone and Chemical Co., Calcite, Mich. Marble Cliff Quarries Co., Marble Cliff, Ohio.

[3] Microscopic examination of the ground stone by A. E. Williams confirms this point.

by the analyses in Table II. A very excellent quality of window glass was made from this material.

The raw materials for sheet glass making must be of the most uniform quality. Experience has proven that even slight variations will produce striae in the finished sheet. Furthermore, in order that it may successfully resist weathering and surface decay (known as "fading") the best window glass is made with a minimum of alkali.[1] In molten glass of this character clay, and other earthy matter, will not readily dissolve. Such foreign matter, partially dissolved, produces "knots," "lines," "strings," and "stones" in the finished glass.

From the point of view of production losses involved, a few bits of clay found in a car lot of ground limestone, would justify the rejection of the entire car lot. A small amount of such foreign matter is fully as much a source of trouble to a window glassmaker as is a little excess "iron" to flint glass making.

In testing a car lot of material for contamination, it is useless to attempt representative samples. In fact, an effort should be made to pick samples for test from suspicious spots, off color stone, or in corners where segregation may have taken place; quite the opposite of regular sampling practice. In testing for contamination a chemical analysis is apt to be unreliable. For example, in a 90,000 pound car lot of ground stone, one handful of clay would amount to less than $^1/_{100}$ of one per cent but even that small an amount of foreign matter would ruin a considerable quantity of sheet glass.

It is obvious that the allowable variation in composition of the raw materials for glass making should not exceed the permissible error in weighing the batch proportions. The maximum error allowable in weighing batch for sheet glass making should certainly not exceed ±0.4%.[2] This limit would permit an error of eight pounds in weighing a batch based on 1000 pounds of sand.

In specifying a limestone it is rather futile to ask a quarryman to produce a stone of a given chemical composition. There are certain objectionable items such as iron, the maximum percentage of which may be specified, but a better practice so far as sheet glass making is concerned would be to determine first whether a quarry exposes a limestone suitable for glass making. A quarry selection and milling routine may then be specified which will enable the *quarry man* to produce the uncontaminated limestone, in a suitable size. In many cases it is, of course, a poor practice for customers to tell operators how to run the quarry. Limestone producers, however, are frequently unfamiliar with the real requirements of the glass trade and welcome any suggestions which will enable them to better satisfy their customers. It is ordinarily impossible to make a complete chemical analysis of every car load of limestone received at a window glass factory, nor is this necessary provided a careful inspection of the material be made in the car for contamination, and traces of foreign matter.

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[1] Eighteen parts Na_2O per 100 parts SiO_2. One of the chief objections to sheet glass made by some methods is the very high alkali content. The high alkali, however, gives a very clear glass free from stones.

[2] Some types of standard equipment will mix batch with an average error well under this limit.

In regard to the use of burned lime versus raw limestone for making sheet glass, there is little published data at hand on which to base a decision, although a considerable amount of window glass has been made from burned lime in the past few years.[1] There is little reason to think that the use of lime effects any material saving in heat or hastens the time of melting.[2] Incidentally, lime is generally more expensive than raw stone as a source of the lime bases.[3]

Items	Limestone	Burned lime
Net cost f.o.b. quarry or kiln	\$2.00	\$8.00
Freight to factory	2.00	3.00
Cost per ton delivered	4.00	11.00
Approximate total CaO and MgO	56%	97%
Cost per ton oxides delivered	7.15	11.35
Extra cost per ton lime bases from burned lime		4.20
Extra cost per ton glass melted 13.5% CaO, MgO		0.567

The extra cost of burned lime over raw limestone is thus seen to be about \$0.50 per ton of glass made.

There is likewise little data on the subject of substitution of dolomite for high calcium stone.[4] By far the larger part of the sheet glass now made in the United States is made from high calcium stone.

In conclusion it may be stated that the proper place to begin the specification of a limestone for sheet glass making is at the limestone quarry. Chemical composition is at best a poor basis for specification. In view of the many very excellent sources of limestone in the United States, a limestone for sheet glass making should certainly contain 97% combined calcium and magnesium carbonates and less than 1% silica. Good window glass can be made, however, from stone less pure. In any case, the ground material must be entirely free from any foreign matter, chert, flint clay, or overburden debris. For ordinary *green* window glass as much as 0.25% iron oxide may be tolerated although in good stone the iron content is generally much lower than this maximum limit. The proper size of the ground stone depends to a great extent on the mechanical equipment for handling the mixed raw materials. If segregation can be avoided, a coarse stone is to be desired[1] not only because it is less likely to be contaminated with foreign matter but also because of the stirring action of the coarse stone in the melting of the batch in the glass furnace.

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[1] Turner, and others, *Jour. Soc. Glass Tech.*, **5** [20], 188 (1921).

[2] Turner, *ibid.*

[3] Estimated extra cost of burned lime over raw limestone for making window glass. The major parts of lime or limestone which appear in the finished limestone are the lime bases CaO and MgO.

[4] Turner, and others, *Jour. Soc. Glass Tech.*, **5**, 352 (1921); **6**, 101 (1922).

WASHINGTON, PA.

NOTE: The author wishes to acknowledge the aid of Messrs. Flint, Shively, Scholes and others in the preparation of this paper.

[1] Past 6-mesh and retained on 30-mesh is a good general size.

DYNAMIC SYMMETRY AS APPLIED TO POTTERY[1]

By Gisela M. A. Richter

ABSTRACT

A presentation of the fundamental principles of dynamic symmetry including an explanation of its mathematics and an analysis of Greek vases. The application of dynamic symmetry as applied to the designing of Greek vases is given.

I am sure that some of you feel that it is rather presumptuous of me to speak to you on dynamic symmetry as applied to pottery, for I am neither a professional potter nor a mathematician. But just on account of my lowly status I may be acceptable to you today; for one of the chief objections against dynamic symmetry is supposed to be its complicated nature. And when a plain average person tells you that she has found dynamic symmetry applied to pottery quite simple, it may have a stronger appeal than if the statement came from an expert potter or mathematician.

My approach to dynamic symmetry was through Mr. Hambidge's work at the Metropolitan Museum of Art. He came to us five or six years ago after having studied the proportions of Greek temples for twenty years or more, and told us that he would like to measure our Athenian vases for he suspected that they would have the same underlying principles of proportion that the Greek temples have.

To me the idea was extremely attractive. I had long felt, as many people who have studied Greek vases doubtless have, that the proportions of the Athenian shapes are so peculiarly satisfying that there must be a definite underlying principle that makes them so; and if by any chance we could find this principle it would be a great discovery; because then we could apply it ourselves. Also it would be interesting to find that such harmonious design is the result, not of slapdash work, but of a system of proportion found also in nature.

Perhaps some of you will think that this is not the way artistic inspiration works. Artistic inspiration, you will say, is something that comes to one suddenly and has to be expressed on the spur of the moment; one cannot sit down with a mathematical mind and work it out. Far be it from me to circumscribe artistic inspiration or to set down rules and regulations concerning it. But as I have come in contact with the mind of the ancient Greeks, certainly an artistic people, it has seemed to me that they were perfectly willing to combine inspiration with law and order; and if they had found some principle of proportion that was in any way useful to design they would have used it. As a matter of fact we know that both in their sculpture and in their architecture they did a great deal of work and spent a great deal of time on just such problems. So when Mr. Hambidge claimed that a definite principle of proportion underlay the design of Athenian vases also, it did not seem to me a preposterous claim.

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[1] This paper was presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, Feb., 1925. (Art and Terra Cotta Divisions.) Further presentation of this subject will appear in another issue of the *Journal.*

Lecture delivered March 17, 1924 before New York Society of Craftsmen, 65 East 56th St., New York.

The Mathematics of Dynamic Symmetry

I will explain first, in a simple and superficial way, the mathematics and geometry used in dynamic symmetry; then show you a Greek vase analyzed according to dynamic symmetry; and lastly the synthetic process of employing dynamic symmetry in designing vases. Throughout I will use Mr. Hambidge's terminology.[1]

Dynamic vs. Static Symmetry

The difference between dynamic symmetry used by the Greeks and static symmetry used by us today is that the former is based on geometry, *i. e.*, on the relation of areas; the latter on arithmetic, *i. e.*, the relation of numbers. In other words, in static symmetry the height of the vase is related to its width in an arithmetical ratio, *e. g.*, as 4 is to 3 or as 5 is to 9.

Dynamic Symmetry is by Areas

In dynamic symmetry the relation is one of areas; and just on that account it makes it easier to use for design. One of the objections sometimes heard against dynamic symmetry is that there are too many possible rectangles and areas. But this is a purely academic objection; for in practice only a small number of rectangles were used together with their logical subdivisions. Very briefly I want to go through this limited number of rectangles. They are the root 2 rectangle, the root 3 rectangle, the root 5 rectangle and the whirling square. On these four rectangles at least 90% of Greek design is based. Let us take them in their order.

$\sqrt{2}$ Rectangle

$\sqrt{2}$ rectangle is produced by drawing the diagonal of a square, using this as a radius, and completing the rectangle (Fig. 1).

AD = sq. $CB = CF$
$AF = \sqrt{2}$ rect.

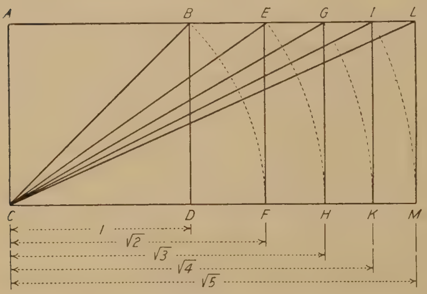

Fig. 1.

$\sqrt{3}$ Rectangle

Use CE in the same figure as a radius, making CH equal to CE and complete the rectangle. AH is a $\sqrt{3}$ rectangle.

$\sqrt{4}$ Rectangle

$\sqrt{4}$ rectangle, which is equal to two squares, is similarly obtained from the diagonal of $\sqrt{3}$ rectangle; and $\sqrt{5}$ similarly from the diagonal of $\sqrt{4}$ rectangle.

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[1] For expositions of Hambidge's theories cf. L. D. Caskey, "Geometry of Greek Vases;" J. Hambidge, "Dynamic Symmetry, The Greek Vase;" J. Hambidge, "Dynamic Symmetry," fifteen plates and text; "The Diagonal," 1919–20, edited by J. Hambidge.

These are the root rectangles which concern us here. Their arithmetical ratios, that is, the proportion in these rectangles of their long sides to their short sides are as 1 is to 1.4141 ($\sqrt{2}$), 1.732 ($\sqrt{3}$), 2.236 ($\sqrt{5}$). These figures are rather complicated, it is true, but they are used only in analysis, not in the actual designing. We need not remember them; we can have a list of them and look at them every time we need them.

Whirling Square

Besides these root rectangles there is the rectangle of the whirling square, as Mr. Hambidge has appropriately named it, which is the rectangle par excellence in Greek design (Fig. 2). It is produced by bisecting one side of a square *AD* at *E*, using *EB* as the radius of a circle and completing the rectangle *AG*. The wonderful property of this rectangle is that as *AC* is to *AF* so *BF* is to *FG;* and if you apply a square *ID* in the rectangle *BG*, the remaining rectangle *BI* has the same proportions, that is, as *BF* is to *FG* so *FI* is to *BF;* and if you apply a square inside the rectangle *BI* again the remaining rectangle has the same proportions; and so on ad infinitum. That is, a square whirls around in this rectangle. For short we will call this rectangle "the whirling square." Its arithmetical ratio is 1.618+.

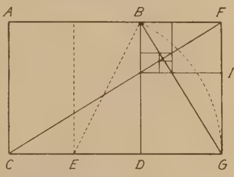

FIG. 2.

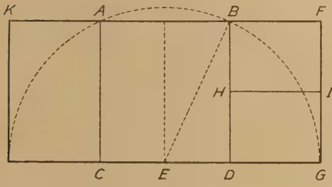

FIG. 3.

If to the large whirling square *AG* you add a smaller whirling square on the other side, namely *KC*, equal to *BG*, the whole figure *KG* is a $\sqrt{5}$ rectangle (Fig. 3). It is the same $\sqrt{5}$ rectangle obtained in a different fashion above; but this shows its relation to the whirling square.

Analysis of Greek Vases

I am not claiming that all Greek vases as you analyze them will turn into simple rectangles of $\sqrt{2}$ and $\sqrt{3}$ and of a whirling square. But analysis has shown that they, or at least the great majority of them, are made up of the multiples and logical subdivisions of these rectangles. In such analysis we must remember that though we can use multiples or divisions, that is, half of $\sqrt{2}$ rectangles or two $\sqrt{3}$ rectangles, we cannot mix them up. If we design in $\sqrt{2}$ we must keep to $\sqrt{2}$; if we design in a whirling square we must keep to the whirling square. Only $\sqrt{5}$ and the whirling square can be combined, for we have seen that the two are intimately related, since a $\sqrt{5}$ is made up of a square and two whirling squares. The whirling square rectangle is the most effective of all rectangles, for it has the most possibilities. For instance, another quality of a whirling square, useful to remember both in analyzing and designing, is that half of a whirling square equals two whirling squares.

Greek Cup

How are these simple principles used in Greek design? Let us take as an example a beautiful Greek cup in the Museum of Fine Arts, Boston (Figs. 4 and 5) analyzed both by Mr. Hambidge and Mr. Caskey, the curator of the classical department in the Boston Museum. Their analysis showed that the rectangle which contained the vase, that is, the rectangle made up of its greatest width and its greatest height, consists of two root 5 rectangles superimposed. (In the handles there is a workman's error.)

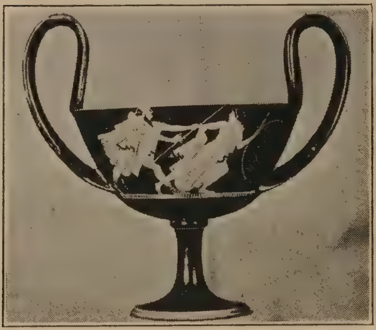

Fig. 4.

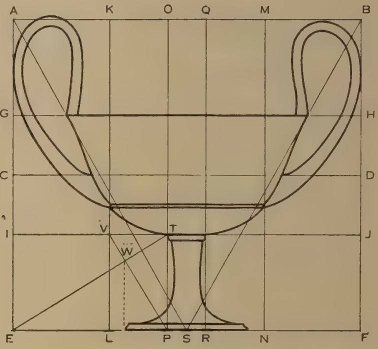

Fig. 5.—Kantharos in Boston Museum.

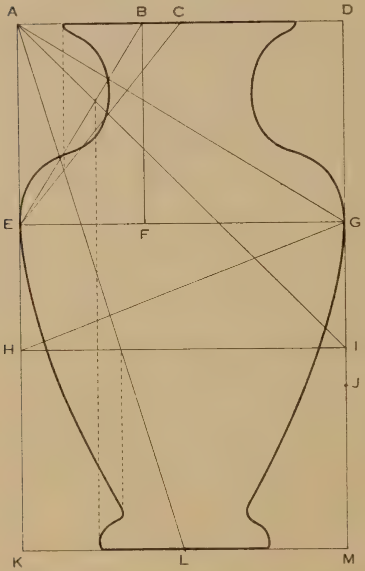

Fig. 6.—Analysis of modern vase. Width = 15.7 cm.; height = 25.4 cm. 25.4 ÷ 15.7 = 1.618 = whirling square. *AI* and *EM* = squares; *AG* = whirling square; *AF* = whirling square.

If four whirling square rectangles are constructed on the four sides of the containing rectangle, namely *AJ*, *EH*, *AR* and *PB*, the overlapping areas *GJ* and *OR* determine respectively the height of the bowl and the width of the stem at its juncture with the bowl.

The diagonals to the two halves of the whole rectangle fix the width of the bowl at the points of their intersection with the sides of the whirling square rectangles. The diagonals *ET* and *VP* to the two whirling squares *IP* and *VP* fix the width of the foot at the point of their intersection.

This is only one example. If you go through Mr. Hambidge's book, "Dynamic Symmetry, The Greek Vase" (Yale University Press, 1920), and Mr. Caskey's book, "Geometry of Greek Vases" (Museum of Fine Arts, Boston, 1922) you will find a large number of

Athenian vases analyzed in this fashion with the same amazing results.

How can we best explain this response of Greek vases to such analysis? Many people believe that it is coincidence and that they would respond equally well to a different analysis. I will only say that if it is coincidence, it is an astonishing one, and that attempts to analyze Greek vases according to the obvious static symmetry have been unsatisfactory, while vases of other countries, for instance the Chinese or Persian, have not been found to conform to dynamic symmetry. The question is still *sub judice*. But I for one feel that if dynamic symmetry—the symmetry claimed to be operative also in nature—is found so readily in Greek design, this may explain the peculiar sense of vitality in Greek art.

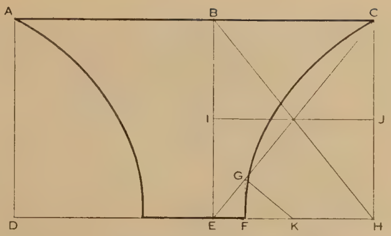

FIG. 7.—Analysis of modern bowl. Width 17.5 cm.; height 9.6 cm.; 17.5 ÷ 9.6 = 1.809 = square plus half a whirling square. AE = square; $BH = {}^1/_2$ whirling square = 2 whirling squares; IH = whirling square.

Designing Based on Dynamic Symmetry

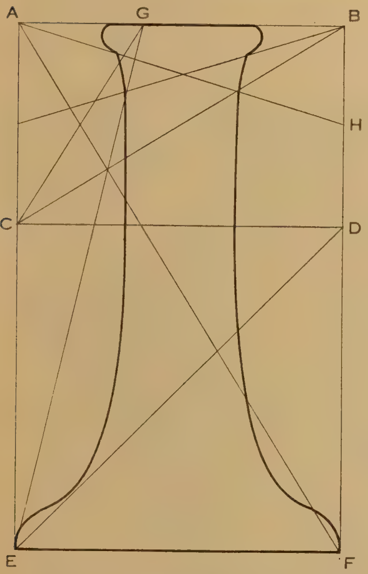

FIG. 8.—Analysis of a modern candlestick. Width 11 cm.; height 17.8 cm. 17.8 ÷ 11 = 1.618 = a whirling square. CF = square; AD = whirling square; GD = square; CG = whirling square; $BH = {}^1/_2\, BD$.

To turn now to the actual designing of vases, I can only tell you the methods I have used in my work, which have seemed to me the most practicable. Doubtless every one who uses dynamic symmetry will do it his own way. First I draw a sketch or several sketches of the pot I wish to make; when I have it about the way I want it I test it by dynamic symmetry. That is, I put it into a containing rectangle, divide the height by the width or vice versa, according to which is the larger measurement, and obtain thereby the ratio. In order to find out whether the ratio is a dynamic ratio I consult a table of these ratios (in which I have put down only the very obvious ones). Let us imagine the height of the vase in our sketch to be 9.7 cm. and the width 17.5 cm. By dividing one into the other we obtain the number 1.804+. This we find is not a dynamic ratio but very near one, for 1.809 is the

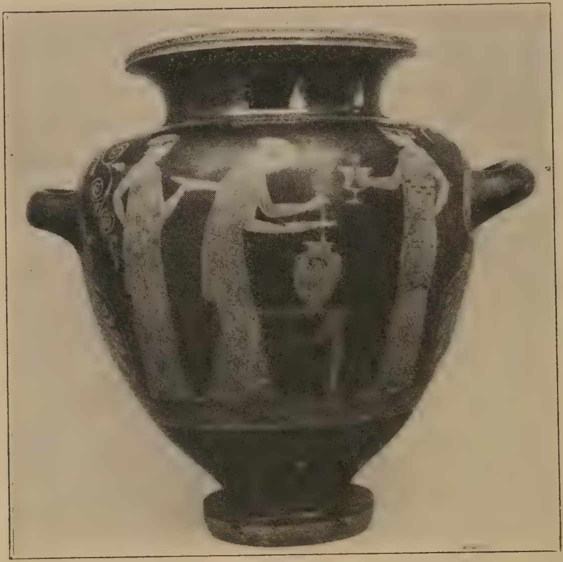

FIG. 9.

ratio of a rectangle made up of a square plus half a whirling square. By changing our sketch a little, varying either the height or the width, we can easily obtain a 1.809 ratio. In my experience the changes I have had to make in my original sketches to make them conform to dynamic symmetry have been slight; but invariably I have felt that I improved my design thereby.

Once you have your containing rectangle according to dynamic symmetry you will think how nice it would be if the width of the foot could be in relation to the width and the height of the vase—and the same with the width of the mouth and of the neck. Your vase might then become, you feel, an interrelated theme. And so you proceed. Figs. 6, 7, 8, are three designs I have tried to carry out myself. All are themes in the whirling square rectangle.

These are very simple designs with few subdivisions. The Greek vases are as a rule strongly articulated (Figs. 4, 9 and 10). They are generally narrowed considerably at the neck and the base

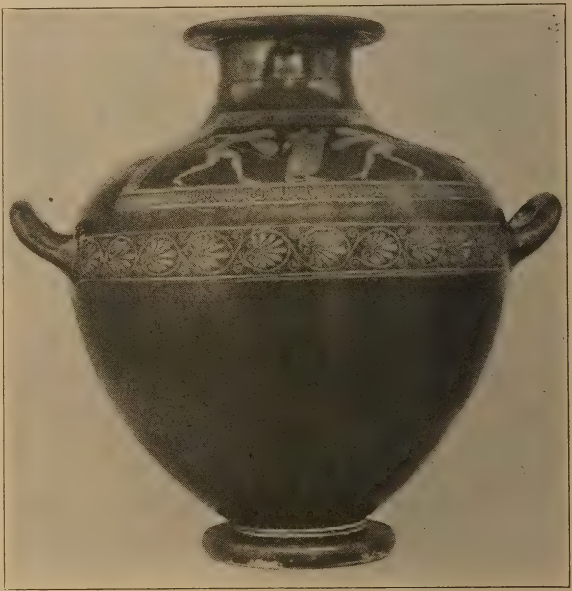

FIG. 10.

of the body, the continuity of the curve is often broken at these points, and handles are regularly added. The interrelation of all these subdivisions must have made a very fascinating exercise, and they give to the Greek vase the properties of an architectural building. How important an element this subtly interrelated proportion is can be seen when we look at modern imitations of Greek forms, which, though they often correspond fairly closely in general outline to their models, almost invariably lack the element of vitality so conspicuous in the Athenian products.

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THE COURSE IN POTTERY AT THE PENNSYLVANIA MUSEUM SCHOOL OF INDUSTRIAL ART[1]

By Edmund deF. Curtis

ABSTRACT

A description of a simple kiln for firing pottery. The kiln consumes about $1.68 worth of kerosene as against $25.00 worth of city gas which had been previously used. Formulas used at the Pennsylvania Museum and School of Industrial Art are given.

The course in pottery at the School of Industrial Art and Pennsylvania Museum has been planned so that at the end of one full year, three three-hour periods a week, the student will have covered sufficient ground to be familiar with all the decorative processes and to have fairly complete control of his tools and materials and should be able to go ahead on his own account without too many discouragements. I do not mean, of course, that he will be a potter but his work ought to be unhampered by lack of knowledge at least.

Equipment The equipment at the school is very simple indeed, a few tubs, buckets, brushes, etc., two small grinding mills, two kick wheels and a kiln that we built ourselves. This equipment is not very elaborate but as we do not make any attempt to cover the commercial field it seems to be enough for a class of thirty.

Pottery Making The clay from Tuckahoe, New Jersey, is soaked overnight in a wash tub, stirred by hand into slip, screened through a rather coarse wire screen and dried in plaster molds to the proper consistency for throwing, coiling or modeling. The student then builds one piece by coiling, using a template to work with. He turns a small bowl upside down out of a solid lump of clay and makes a one piece mold from this original. The next exercise is to turn a vase shape from a plaster cylinder and from this make a plaster section mold.

He casts with the slip into these molds and while the pieces are still plastic trims them and perhaps re-shapes them on the wheel.

Throwing is practiced throughout the year.

The theory of glazes, with enough chemistry to serve as a background, is gone into so that the student is able to make up a formula and work out the batch weights from it and really understand enough of the functions of the different materials to reason himself out of trouble.

The glaze is ground in the ball mills using two parts water to one part gum solution. The latter is made by dissolving two pounds gum arabic in ten quarts of water and straining. The glaze is applied to the unfired clay by dipping, brushing or spraying. The piece must be bone dry and is first plunged quickly into water and then glazed and dried and fired.

The students do all the work themselves and this much of the course gives them a pretty good understanding of the different methods of making original pieces and reproducing them. Most of the pieces used for practice are cast because I find that if they are working on a built piece they are afraid of spoiling it and that is rather a hindrance in getting control of the clay and glazes, and I think the trimming helps, with the wheel work, which of course is the slowest for them to learn.

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[1] Recd. Dec. 30, 1924. This paper was presented for use at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, Feb., 1925. (Art Division.)

Decorating From this point on for a month or so the work is divided up among the class into problems so that each one does a part of the work and benefits by the work of the others. The different methods of decorating—slip painting under a transparent glaze, painting on the unfired cream or white enamel, incised line, relief decoration, color values obtained by flowing glazes or by spraying, and studies of glaze formula variation and temperature—are all treated in this way. The student goes on from this point with the type of work that appeals most to him and uses the rest of the time in obtaining as much proficiency as he can with a very excellent library at the school and both the Pennsylvania Museum and the University Museum to help him get that intangible feeling for line and color that is so necessary in pottery.

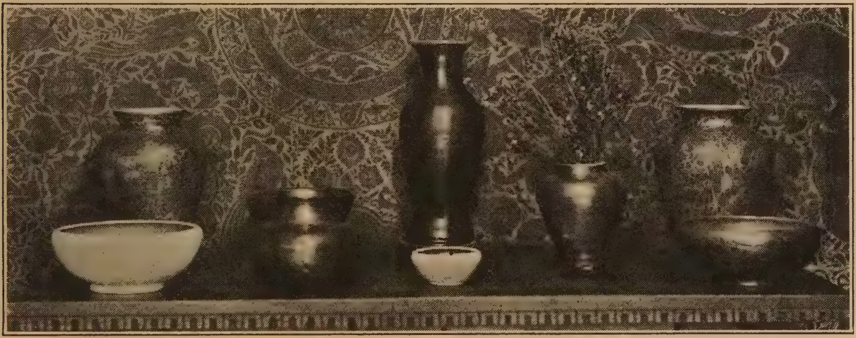
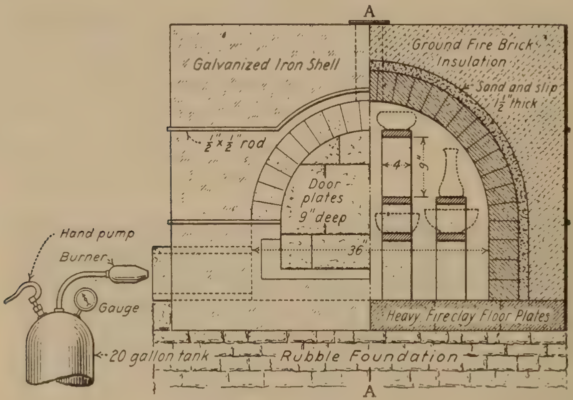


Fig. 1.

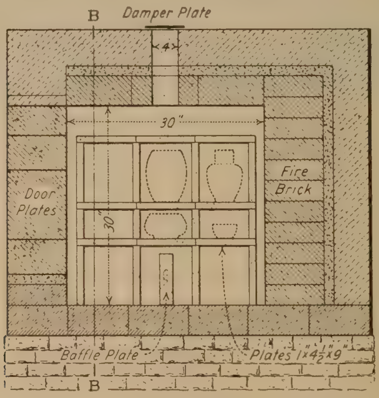
Records We are trying to make the work cumulative so that each class can go ahead with new problems instead of going over the same ground each year and consequently are keeping the samples on small tiles with the formula, history, temperature, etc., marked over them.

The Kiln In carrying out our plan to cover as much ground as possible from the technical standpoint we found that a small kiln that could be fired often suited the conditions and as the kiln we had been using consumed $25.00 worth of city gas it was going to be pretty expensive to fire once a week. So in the interests of economy we built a Conestoga kiln similar to the kilns I use in my own work which uses, for a 3 ft. x 3 ft. x 30 in. space about $1.68 worth of kerosene. This holds just as much pottery as the gas kiln but the ware is fired in the open flame and is not protected in any way by saggers or muffles or tubes. A brief description of the kiln will probably be interesting.

On a suitable foundation about waist high from the floor a single course of fire brick is laid four and one-half inches thick, four bricks high laid up with thin fire clay mortar; over this an arch is turned using mortar half way up and the balance dry; over this shell a stiff mixture of sand and fire clay mud about an inch thick is spread. Then one end of the arch is closed with brick except for the burner hole, about ten inches square and the other end is used for the door and is bricked up each time. A galvanized iron shell is then made going around three sides of the kiln about six inches from the brickwork and the space filled with ground fire brick for insulation. Inside the kiln some brick are stood on end leaving as much open space as possible for the flame and with these as supports and one-inch plates as shelves the ware is loaded. It is usually necessary to give the inside of the kiln a heavy coat of glaze before using it. The door is then put in and the burner started.



Front Elevation showing Section at Line B-B



Side Elevation showing Section at Line A-A

FIG. 2.

The burner is of the atomizing type and has to be preheated which takes only a few minutes; it is connected to a tank holding twenty gallons of coal oil and is kept at a pressure of 40 pounds by means of a hand pump.

A stack is not necessary with these kilns except for ventilating purposes. The most difficult thing about the kiln is bringing the heat up slowly enough, but unless there are very large pieces in the kiln one hour at the lowest rate the burner will go is enough, and then the temperature may increase gradually until by the end of two hours it is going full blast, which makes quite a lot of noise but does no damage. The kiln may be finished to cone 3 in about nine hours and the control of the atmospheric condition inside the kiln is positive and immediate which makes many things possible that are very uncertain in the usual pottery kiln. It may be fired twice a week and of course the burner is portable and will handle one kiln a day if there were that many to fire.

I do not know what troubles would develop with other clays and glazes than the ones we use but so far I find at the school and in my own work that aside from carelessness the loss is no more than with other types and of course the repair bill for this type is almost nothing as there is no floor, etc. The burner can be handled so that a heavy reducing condition may be cleared up in less than a minute and delicate overglaze colors or lusters may be fired with no loss from smoking. I think it took two of us four days to build this kiln and the brick and burner came to something like $150.00.

FORMULAS USED AT PENNSYLVANIA MUSEUM AND SCHOOL OF INDUSTRIAL ART, PHILADELPHIA, PA.

White enamel	
White lead	129
Whiting	25
Eureka Feldspar	83
Kaolin	13
Flint	32
Zinc	12
Tin	20

Black enamel	
White lead	180
Flint	50
Kaolin	20
Tin	15
Manganese	15
Cobalt	7
Copper	5
Chrome	½

Turquoise	
White lead	48
Whiting	24
Feldspar	38
Kaolin	10
Flint	57
Tin	10
Soda Bicarb	56
Borax	24
Copper	6

Silver green	
White lead	103
Whiting	25
Feldspar	111
Zinc	12
Kaolin	13
Flint	27
Tin	12
Copper	4½
Cobalt	½

Any of the formulas given in Prof. Binns' "Potter's Craft" may be used.[1]

These glazes are mixed with the right quantity of $^2/_3$ water and $^1/_3$ gum solution mixture and are used without decanting if possible, on unfired ware.

The type of burner, size and shape of kiln and capacity of tank must be pretty carefully planned but once it is working it certainly is nice to be independent of weather conditions and melting floors. I do not imagine that it would be economical if the class were large enough to require a coal fired kiln but for this particular course it is most satisfactory.

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[1] "The Potter's Craft," D. Van Nostrand Co., 1910.

The Training Given When the student has completed the full course he is supposed to be able to write a paper explaining in detail what, if he had a shop of his own, he would make, how he would make it and where and how he would sell it. It seems to me that there is a future for the potter craftsman. Certainly there is no other material that will lend itself to so many uses and types of decorative methods than clay and a great many articles of everyday use now made by machinery and of metal might easily have the craftsman's touch added and be produced in terra cotta or faience without making the price prohibitive.

The great stumbling block so far in developing this field has been the cost of equipment and the lack of exact knowledge so that the loss may be held down to a reasonable figure and we hope that the work done at the School of Industrial Art will be sufficiently varied in type and use and of a high enough standard of quality to prove that the field may be entered with no great outlay of capital and with a reasonable chance of success.

Conestoga Pottery
Wayne, Pa.

FURTHER EXPERIMENTS IN THE PROBLEM OF THE TURQUOISE ALKALINE GLAZE[1]

By Myrtle Meritt French[2]

ABSTRACT

The blueness of the glaze was found to be influenced by the biscuit of the body, the amount of copper used and the fire of the glaze. Indications of small tests were not always dependable. Encouraging experiments are being made to obtain a raw turquoise on body which will be impervious at cone 04.

Certain results obtained during experiments for the previous article[2] on this subject suggested that a bluer turquoise might be obtained over an immature body than could be produced over a well-fired one. Being desirous that the process should be simple and practical it was decided to try the glaze on the raw body, also to raise the firing point to cone 04, thus making it possible to put the turquoise alkaline glaze in the same kiln with regular low fire work. The desirability of obtaining an impervious body was not lost sight of.

The following new bodies were weighed with the idea of increasing ball clay to make more plastic, and flint to further diminish crazing possibilities.

	No. 10	No. 11	No. 12
Tenn. Ball Clay No. 9	18	28	28
Eureka Feldspar	10		
Kryolith		4	
Flint	64	68	68
Whiting	8		4

Besides those, clay numbers 3, 4, 5, 6, 8, of the former report were prepared. They were as follows:

	No. 3	No. 4	No. 5	No. 6	No. 8
Cornwall Stone			17		
Tenn. Ball No. 9	18	14	17	13	18
Georgia Clay				19	
Eureka Feldspar	10	19			14
Kryolith	8	8	6	6	6
Flint	64	59	60	62	62

Over these raw, dry bodies was applied the same fritted glaze given in the earlier report—namely:

$$\left.\begin{array}{ll} Na_2O & .6 \\ K_2O & .1 \\ Ca_2O & .3 \end{array}\right\} \quad SiO_2\ 2.8$$

To this was added 27 grams of black copper oxide to the batch.

For a few hours after the tests came from the kiln none was crazed; but at the end of several days, all had crazed slightly except on the three new bodies.

The next experiment was to determine the amount of copper which would give the bluest color. The above glaze was used as a test. Five batches were fritted, containing the following amounts of copper: 27

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[1] Recd. Jan. 26, 1925. This paper was presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, Feb., 1925. (Art Division.)

[2] Continuation of an article published in *Jour. Amer. Ceram. Soc.*, **6** [2], 405 (1923).

gms., 15 gms., 12 gms., 6 gms., 3.5 gms. The superior color ranged from 6 to 12 gms. Lower than that the glaze was not as strong a blue and above 12 gms. the glaze became greener. All were tested on raw clay body No. 12.

At this point, the information gained from the foregoing tests was applied to the making of pieces as tall as eight inches. It was found first that clay bodies containing as high as 6% kryolith were very sensitive to overfire, though when the exact maturing point was reached (and no more) the pottery was satisfactory; second, that the blueness of the same glaze on the same clay fired in the same kiln at the same cone varied considerably with different kiln firings; third, that out of several pieces built of clay No. 12 not one was really satisfactory; the body shivered when matured and leaked when immature, however, the color was the finest blue of all, further indicating that the immature body tends to give a better color; fourth, that often a glaze which would not craze on a small piece would do so on a larger one; and fifth, that the fritted alkaline glazes are always more or less troublesome, because of their tendency to settle into a rock-like mass. Free flint, magnesium sulphate, and mucilage tend to counteract this quality but it is always something to be dealt with—especially when the glazes are to be dried out.

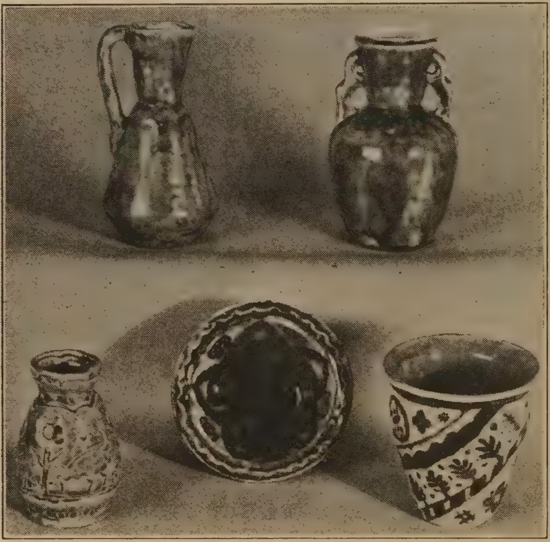

Fig. 1.

Studying the problem from the historical point of view, it seems scarcely probable that the Egyptians or early Persians withstood all these difficulties to produce their bluest turquoise glazes. It is doubtful that they biscuited their ware and it seems likely that the number of materials included in their glazes would be limited. Upon these assumptions, the problem is being approached from an entirely different angle; namely, that of a raw body glazed with a raw glaze compounded as simply as possible and fired at cone 04. A few extremely gratifying results have been obtained, but sufficient material is not at hand to justify a definite report at the present time.

Art Institute
Chicago, Ill.

OBSERVATIONS ON PINHOLING IN CAST WARE[1]

By R. W. Hemphill

ABSTRACT

Some effects of foreign matter, dampness, ball clay content, sponging, dust and drying are shown on pinholing in cast ware.

In our factory we have to be very careful about pinholes, as a piece of cast ware with a single pinhole must either be retouched and refired, or thrown out as scrap. No cast ware can leave the plant with a pinhole, as the forms are used in making dipped rubber goods and a pinhole will cause a blister in the rubber, when it is cured.

Causes of Pinholes

Solid Carbon Of course there are some general causes for pinholing that everyone familiar with casting knows, such as air in slip, or something burning out of the body. Years ago, before we had filterpresses, we had considerable trouble with pinholes and traced it to some clay that had been shipped in a car that evidently had been loaded with wheat or oats on the trip before. You can well imagine what happened.

Damp Molds Dampness often causes pinholes in several different ways. Damp molds are bound to cause them as a damp mold will not properly absorb the air out of the slip, when it first is poured into it. This point was very forcibly brought to the writer's attention when experimenting with a mold made so that the top part or cover was too thin. The first casting each day would be all right, but the second and third would be full of pinholes at that part next to the thin part of the mold. The rest of the casting would be free from pinholes. This was no doubt due to the thin part getting saturated or nearly saturated before the rest of the mold, thus trapping the air in the slip.

Contact with Damp Cloths I have also observed that covering cast ware with cloths that are too wet, will cause pinholes where they touch the casting. We experienced this trouble and it took us quite a while to trace it back to the cause. Every Tuesday our ware would show up pinholes on the top side after the glaze was applied. Of course, it took some time to notice that this trouble occurred every Tuesday. We then traced it back and found that on Saturday afternoon, Saturday's castings were covered with wet cloths to keep them damp so that they could be held over and sponged Monday. This ware was then dried Monday night and glazed Tuesday. By covering the

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[1] Recd. Dec. 22, 1924. This paper was presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, February, 1925. (White Wares Division.)

ware first with dry cloths, with the damp cloths on top, trouble of this nature was overcome.

Too Slow Drying Slip Some slips seem to dry too slowly in the molds. It has been my observation that this is a cause for pinholes as it, in some way, traps the air. We had one body that caused considerable trouble this way and our ware was full of pinholes. After the ware was cast and the slip poured out, the ware would have the proper thickness in the mold, but would stay soft and slushy in the mold.

Even after the ware seemed to be stiff, the least little movement or jar would make it again soft and "runny." As previously stated, this seemed to produce pinholes and was overcome by adding a small amount of dark ball clay so that the ware dried properly in the molds.

Too Low Ball Clay Content I have observed that a slip too low in ball clay will pinhole more than one a little higher in ball clay. We cast with as high as 23% ball clay with very good results, but when we get down around 10% ball clay, we get a casting that is literally full of pinholes. Of course, this may be from some other cause that I do not know about, but indications seem to point to the ball clay content.

Incorrect Sponging Then, of course, there are some general points to be brought in about the handling of the cast ware after it has been cast. We find that sponging can be done most advantageously when the ware is leather hard. Of course, the ware must then be properly dried before applying the glaze.

Dust All dust must be removed before the piece is glazed and this can be done by blowing it off, and sponging, or dipping the ware in water. The ware should be cooled down to room temperature before the piece is sponged or dipped in water, and the water should not be below room temperature. Of course, if this operation is done, while the ware is still warm, I suppose the water could be heated up so that the results would be the same. We found that dipping the warm ware caused the ware to crack along the seams where the mold comes together and that it also caused pinholes to appear as blisters on the surface of the green ware. The difference in temperature seems to cause the outer layer or crust of clay to separate and to magnify any defects in the clay body that ordinarily would not show up even in the fired ware.

Ware Not Dry before Glazing Then the ware must be thoroughly dried after the sponging or dipping in water, before the glaze is applied; for if it is not the small defects will then be brought to the surface and bad results obtained.

In glazing the ware, the glaze must not be too thick and the piece must not be held too long in the glaze. Of course, this all applies to single fired ware. If the glaze is too thick or the piece held too long in the glaze, imperfections will again be magnified.

Ware Must Be Dried before Firing

The ware must also be thoroughly dried after glazing before going into the kiln, as any steam forming under the surface will cause pinholes and defects in the glaze. I might add here that we get much fewer pinholes in single fired ware than biscuit and glost fired ware, and always use the single fire where that method is possible. We can take two pieces cast the same and the single fired piece will be perfect while the two fired piece will be full of pinholes.

Questions

There are many things I would like to know about casting and some are as follows:

Why is it that two slips will apparently cast and work up the same, yet one body will be literally full of pinholes and the other nearly perfect? Also, why will two bodies that have the same total shrinkage when pressed by the dry process, have entirely a different shrinkage, with the same amount of water added, when cast?

Specifications for a Good Casting Body

The body must of course cast and dry properly. It must sponge up smoothly. Some bodies when sponged will be full of ridges and others will sponge up smoothly. Then the body must take a good glaze and fire white. The castings must of course be right for size and must not warp out of shape either in drying or firing. I find that a body high in flint will stay straight while drying and firing, whereas one low in flint will warp considerably. Of course, this is an old theory and no doubt true. Last, but not least, the body must not pinhole.

In closing, I wish to say that it is surprising how unsightly a piece of cast ware can be made to look, unless the utmost care and painstaking effort is used during the process of manufacture.

Colonial Insulator Co
Akron, Ohio

SOME FORMS OF SULPHURING ON EARTHENWARE GLAZES[1]

By Thomas A. Shegog

ABSTRACT

A discussion is given of the sources and effects of soluble sulphates on the glaze and body.

The terms "sulphuring," "starring" and "feathering" are used to denote the formation of a scum or film of undissolved sulphates on the surface of a glaze. As Seger[2] has pointed out sulphates may be introduced through the body, the glaze, the water or the fuel.

Sulphates in the Body

Only those soluble in water need be considered; the insoluble ones are harmless. The soluble sulphates are deposited on the surface of the ware during drying as a crystalline scum, especially on corners and sharp edges where evaporation is most rapid. In the bisque kiln this scum is fired on and often shows as a glossy patch. When the piece is dipped and fired in the glost kiln these sulphates may be dissolved by the glaze, and may cause "crawling," or "rolling" or "creeping" of the glaze by preventing it from coming into sufficiently close contact with the bisque body.[3]

"Crawling" is especially liable to occur on vitreous sanitary ware where the glaze cannot adhere to the body as firmly as in ordinary non-vitreous ware. Some years ago the writer had a troublesome case of glaze crawling on the foot of closet-bowls. The trouble was stopped by sandpapering or sandblasting the foot of each bowl before dipping. The same results were achieved more easily by sponging each foot in the clay state after the piece was thoroughly dry.

Likewise it is this scum of sulphates that causes dry edges on plates.

Sulphates from the Fuel

All fuels except wood and natural gas contain sulphur. In whatever form it may occur it is converted during firing into sulphur dioxide, a variable proportion of which is further oxidized to sulphur trioxide. This trioxide, in the presence of moisture, may be deposited in small vesicles on the saggers and the ware in the cooler parts of the kiln at the beginning of the firing and, in the glost kiln, causes, what I have called, "polka-dot" sulphuring. This consists of small dull spots or rings which may be distributed all over the surface of the flat ware, but are more frequently concentrated around the pin-marks, since the saggers at that part are porous and consequently permeable by water-vapor and kiln gases.

The "polka-dot" form of sulphuring consists of dots or rings of sulphate

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[1] Recd. Jan. 13, 1925. This paper was presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, Feb., 1925. (White Wares Division.)

[2] "Collected Writings," **2,** p. 647.

[3] Seger, *loc. cit.,* **2,** p. 1147.

scum, each dot marking the position where a vesicle of acid-laden moisture condensed on the ware during the initial stages of the firing in the glost kiln.

With a good mechanical draft it is possible to avoid this condensation to a great extent, but the draft of the ordinary round up-draft kiln is naturally slowest at the beginning of the firing.

Mellor[1] (referring to the ordinary sulphur scum) states that sulphuring is most likely to occur near the end of the firing when the fireman shortens the flame to get the bottoms and so admits a large excess of air to the tops.

Mellor produced a crystalline film of sulphates on glazed tile by heating them in a porcelain tube through which air charged with sulphur trioxide gas was passing, also by re-firing ordinary glazed tiles in a muffle with alum, which on strong heating gives off sulphur trioxide. I have convinced myself, however, that the conditions under which the polka-dot form of sulphuring occurs are present only in the early stages of the firing while the ware in the cooler parts of the kiln is cold enough to permit the condensation of water upon it.

Sulphates in the Glaze

If present in sufficient amount both soluble and insoluble sulphates in the glaze may cause trouble since both will be dissolved by the melted glaze.

According to Seger[2] a bi-silicate glaze can dissolve about 4% of sulphates, while a tri-silicate glaze can dissolve only about 2%. It might seem from this, that reducing the amount of silica in the glaze should reduce, or prevent, sulphuring. This has often been tried but in my opinion it is of doubtful efficacy for, as is well known, the lower the silica in the glaze, the more vigorous is the attack of the glaze on the silica of the body and it seems to matter little whether the glaze is originally high in silica or takes it up from the body.

For sulphuring to take place, it is not necessary for the entire thickness of the glaze to be saturated with sulphates, for as Mellor states: "If the sulphates developed on the surface have not time to diffuse into the rest of the glaze, a film of glaze saturated with sulphates may be produced on the surface of the ware and this on cooling may produce crystals of sulphates." Owing to the high viscosity of the glaze and the consequent slowness of diffusion in it, the relatively high-silica layer formed nearest the body would be slow in affecting the surface and for that reason the expedient may have some merit; for the same reason, however (the slow diffusion), sulphuring can occur when there are not enough sulphates present to saturate the whole thickness of the glaze, so the influence of high or low silica content of the glaze on sulphuring can easily be exaggerated.

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[1] J. W. Mellor, "Sulphuring and Feathering of Glazes," Part II, *Trans. Ceram. Soc.* (Eng.), **6,** [1] (1906–7).

[2] Seger, *Loc. cit.*, **2,** p. 646.

Example of Sulphuring

1. Sulphur in Glaze Water

The first case of sulphuring to which I wish to call attention occurred in an oil-fired Dressler tunnel kiln used for glost firing. It was a case of ordinary scum sulphuring but a very severe one.

The top saggers in this kiln were not covered and none of the saggers were wadded. It was found that the top piece of flat ware in every top sagger became completely coated with a scum giving a rather pleasing matt effect in some instances, while many pieces showed the well-known sulphur wrinkles and blisters. Pieces lower down in the bungs were more or less affected, generally near the edges. This condition had continued for some three months. Later on (the Dressler kiln having been shut down for repairs), the ware was fired, some with oil and some with coal, in round glost kilns, with the result that very large losses were incurred from sulphuring, all kilns being affected alike.

After examining the raw materials and the fuels in use, I concluded the cause of the trouble must be sought in the water used in the glaze mills. I found it was the practice to use the same water over and over again, and that to each charge of glaze, a small quantity of Epsom salts was added to help to float it. The repeated re-use of the water naturally brought about a concentration of the Epsom salts. The water from the glaze agitator contained soluble sulphates equivalent to 192 grains of sulphuric acid (H_2SO_4) per gallon.

To stop the trouble, the use of the Epsom salts was discontinued and instructions given that fresh well water be used with each batch of glaze. It was 10 days before a distinct reduction was shown, the soluble H_2SO_4 content then amounted to 161.6 grains per gallon. One week later, it had fallen to 47.2 grains, at which point the sulphuring ceased, and one week later it was down to 2 grains per gallon.[1]

No sulphuring has since occurred at this plant either in the tunnel kiln or in the round kilns except on one occasion about a month later when, owing to a scarcity of dipped ware, the schedule of the kiln was increased from 60 minutes to 90 minutes, and the draft was (by accident) simultaneously cut down to about half normal. Before the normal draft could be restored, a few cars of ware were sulphured.

The glaze on this plant is pumped over, not siphoned.

I may add that the water from the filter presses (which was used over and over again), contained, when I tested it, soluble sulphates equivalent to 23 grains of sulphuric acid per gallon, a quantity which, of itself, seems to be harmless. This case occurred seven months ago.

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[1] The H_2SO_4 content of the fresh well water used in the glaze mills was 1.7 grains per gallon.

2. Another Case Re-using Water

The second case occurred almost simultaneously at another plant where round, up-draft, oil-fired glost kilns are in use. It first appeared occasionally as small, dull dots more or less evenly spaced on one or two pieces of flat ware in a kiln. Soon it appeared more frequently and finally was of regular occurrence on most of the flat ware around the pin marks. No method of firing seemed effective in preventing it. This was the first appearance of the polka-dot sulphuring.

As in the other plant, the same water was being used over and over again for grinding the glaze and Epsom salts used to float it.

3. The Same Glaze, but No Sulphuring

At a third plant using the same glaze and materials we did not find sulphur trouble, but at this plant no Epsom salts was used in grinding each batch of glaze and the water was not re-used. A sample of water taken from the glaze-agitator at this plant contained soluble sulphates equivalent to 32 grains of H_2SO_4 per gallon and the glaze was pumped over into the agitator instead of being siphoned.

Limit of Permissible Sulphur Content in Glaze

Being satisfied that the mottled, or polka-dot effect in the second case described was sulphuring, the use of Epsom salts was discontinued and fresh water used for grinding each batch of glaze. The soluble sulphates calculated to grains H_2SO_4 per gallon in the glaze water each succeeding week was:

	Grains		Grains
Original	252.2	Fourth week	97.0
First week	184.4	Fifth week	66.0
Second week	142.7	Sixth week	40.4
Third week	187.0		

At this point the trouble ceased. With the type of glaze used, below 45 grains H_2SO_4 per gallon seem to be harmless.

The sudden increase at the end of the third week was puzzling till I found that the steam used for siphoning over the glaze sometimes contained the equivalent of 102.6 grains H_2SO_4 per gallon while on other occasions it was entirely free from sulphates.

The town water used in the glaze grinding in the second case described had a H_2SO_4 content varying from 1.72 to 9.75 grains per gallon (alum is used to purify). By firing ware from the affected plants at different other plants it was proved that the cause of sulphuring was not from the fuel or firing conditions. All the trials made, pointed to the soluble sulphates in the glaze as the cause of the trouble in both cases. Had it not been that the weekly H_2SO_4 determinations kept us informed of the variations in the amount present, it is doubtful if we should have had the patience to persevere. Without this information we should probably have concluded that we were on the wrong track and have sought the cause of our trouble in some other direction.

Distinction between Sulphur Scum and "Polka Dot"

The presence of moisture in the kiln and its condensation on the ware is beyond doubt a prerequisite for polka-dot sulphuring. This moisture may be derived from damp ware, the wads, the fuel, and other sources. The sulphates which actually cause the dot must come from the combustion of the sulphur in the fuel and be sufficient, when added to the dissolved sulphates already present in the glaze, to more than saturate these particular spots, being concentrated there in the water vesicles.

The sulphur scum is formed at a later stage of the firing from sulphur trioxide fumes passing through the hot kiln.

The "polka-dot" sulphuring could be produced by an amount of SO_3 insufficient to form a noticeable scum, hence the presence or absence of condensed moisture on the ware must be the determining factor.

Air versus Steam Atomizing Oil Burners

At a third plant experiments on different fuel-oil burners were made. In two types steam was used instead of air for atomization of the oil. No sulphur trouble had at any time occurred at this plant, but in all four firings with steam atomizing burners, polka-dot sulphuring appeared in considerable quantity while no trace appeared when air-atomization was used. Since water from the glaze agitator at this plant showed only a faint trace of sulphates, the sulphuring obviously was due almost entirely to the sulphur trioxide derived from the oil fuel and concentrated in the water vesicles as already described.

Sulphuring in Decorating Kiln

A roughening and darkening of the glaze was found on ware from the decorating kiln on the affected plants. The trouble has been experienced by many but I have not found any explanation for it. I believe it to be an effect of the presence of sulphates in the glaze.

It is well known that up nearly to the end of the decorating kiln fire, the atmosphere of the kiln is strongly reducing owing to the presence of the oils and size on the decals and the usual absence of efficient ventilation of the kiln. I think it very probable that under such conditions the sulphates in the glaze are reduced to sulphites, at least near the surface of the glaze layer. This reduction implies the formation of minute bubbles of oxygen gas in the slightly softened glaze, near the surface and I believe this to be the cause of the roughening of the affected parts. The dark discoloration is almost certainly due to the reduction of lead in the glaze.

The effect appears only in the hottest part of the kiln near the middle and most frequently around the edge of glaze curtains. I regard it as a kind of surface spit-out due to sulphur and developed under reducing kiln conditions. When the sulphuring in the glost kilns ceased this trouble ceased also and has not re-appeared.

R. G. Cowan[1] of Alfred, N. Y., attributes spit-out in general to the presence of sulphur and explains it in a somewhat similar way. I cannot agree that sulphur is the usual or even a common cause of the ordinary form of spit-out since this fault occurs in very many cases when there is no indication of sulphur trouble, and I have always found the particular form of spit-out which I attribute to sulphur, associated with a darkening of the glaze on the affected parts which is not characteristic of ordinary spit-out. Also, the roughness of the darkened surface is much less pronounced than is usual in regular spit-out.

Conclusions

1. Sulphuring of glazes may manifest itself in two forms:

(*a*) Polka-dot sulphuring, which occurs early in glost firing and is due to vesicles of acid-laden moisture condensing on the surface of the glaze.

(*b*) Scum or film sulphuring which occurs later in the firing when the kiln is too hot for moisture to condense on the ware.

2. The use of soluble sulphates, *e. g.*, magnesium sulphate, to float the glaze may cause sulphuring if the same water is repeatedly re-used in the glaze mills.

3. If the amount of soluble sulphates in an earthenware glaze containing about 2.5 equivalent of SiO_2 be less than about 40 grains per gallon (calculated as H_2SO_4) they appear to be harmless under normal firing conditions.

4. Sulphuring in either form may occur with a very slow kiln draft and a long glost fire when under normal firing conditions it would not appear.

5. The use, in glost firing, of steam atomizing fuel oil burners conduces to the occurrence of polka-dot sulphuring.

6. The roughening and darkening of the glaze which sometimes occurs in the decorating kiln is a sulphur effect developed under reducing kiln conditions.

SEBRING POTTERY CO.
SEBRING, OHIO

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[1] "Spitting-Out a Phenomenon of the Decorating Kiln," *Trans. Amer. Ceram. Soc.*, **9**, 493 (1911).

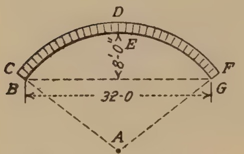
DESIGNING BANDS FOR ROUND KILN CROWNS[1]

By B. W. Willson

ABSTRACT

Selecting bands for round kilns is largely a rule of thumb matter, practice ranging from a few light bands to a jacket enclosing the entire kiln with openings for wickets and fire boxes. The purpose of this paper is to analyze stresses in and thrust caused by a round kiln crown and select bands to with stand these stresses.

Volume and Weight of Crown



Diameter of kiln, 32′ 0″.
From spring of crown, to top of crown, 8′ 0″.
Crown, 9″ fire brick.
2″ platen of common brick.
Required size of band at skew-back.

Fig. 1.

For our problem we shall select a kiln (Fig. 1) 32 feet in diameter, with a rise from spring to top of crown equal to one-fourth of the diameter, or 8 feet, the surface of the crown being a portion of the surface of a sphere. The crown is built with nine inches of fire brick and a two-inch platen of common brick.

To find the volume of the crown and therefrom its weight is our first problem. To find the radius of the sphere, whose surface coincides with the under side of the crown refer to Fig. 2.

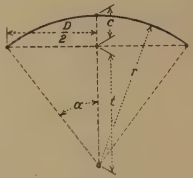


Fig 2.

From plane geometry:

$$r^2 = \left(\frac{D}{2}\right)^2 + t^2$$

$$t = r - c$$

$$\therefore r^2 = \left(\frac{D}{2}\right)^2 + (r - c)^2$$

$$r^2 = \left(\frac{D}{2}\right)^2 + r^2 - 2rc + c^2$$

$$r = \frac{\left(\frac{D}{2}\right)^2 + c^2}{2C}$$

Substituting values:

$$r = \frac{16^2 + 8^2}{2 \times 8} = 20$$

$$\alpha = \sin^{-1}\frac{D/2}{r} = \sin^{-1}\frac{16}{20} = 53° \; 8'$$

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[1] Received Jan. 15, 1925. This paper was presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, Feb., 1925. (Heavy Clay Products Division.)

The volume of the crown may be found by several methods. In this calculation the theorem of Pappus will be used, *viz.*, "The volume of the solid of revolution generated by a plane area revolved about a non-intersecting axis in its plane is equal to the product of the area and the length of the path traced by the centroid of the area."

The area of a sector of a circle is $^1/_2 r^2\alpha$.

To locate the centroid of the sector of a circle consider it placed as in Fig. 3 with the X and Y axes as indicated. From symmetry, the centroid will be on the X axis.

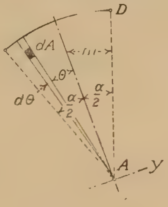

FIG. 3.

$$\therefore \bar{y} = 0$$

To determine $\bar{x}$.
From mechanics

$$A\bar{x} = \int x\,d\,A$$
$$A = {}^1/_2\, r^2\alpha$$
$$dA = \rho d\rho d\theta$$
$$x = \rho\cos\theta$$

$$A\bar{x} = {}^1/_2 r^2\alpha\,\bar{x} = \int_0^r \int_{-\frac{\alpha}{2}}^{+\frac{\alpha}{2}} \rho^2 \cos\theta d\rho d\theta$$

$$^1/_2 r^2\alpha\,\bar{x} = 2\sin\frac{\alpha}{2}\int_0^r \rho^2 d\rho$$

$$^1/_2 r^2\alpha\,\bar{x} = 2\sin\frac{\alpha}{2}\,\frac{r^3}{3}$$

$$\bar{x} = \frac{4r}{3\alpha}\sin\frac{\alpha}{2}$$

The perpendicular distance from the centroid to axis $AD = M = \bar{x}\sin\frac{\alpha}{2}$.

The length of the path of the centroid during one revolution is $2\pi\,\bar{x}\sin\frac{\alpha}{2}$.

The volume becomes

$$^1/_2 r^2\alpha \times 2\pi\frac{4r}{3\alpha}\sin\frac{\alpha}{2}\sin\frac{\alpha}{2}$$

which simplifies to

$$\frac{4}{3}\pi r^3\sin^2\frac{\alpha}{2}$$

Returning to Fig. 1 revolve plane surfaces ACD and ABE about the axis AD and the difference between the volumes thus found will be the volume of the kiln crown. The volume thus found is 1058.62 cubic feet and weight at 125 pounds per cubic foot is 132,327 pounds. Computations are appended.

Thrust of Crown

Referring to Fig. 4, the line of thrust caused by the weight of the crown will be normal to the face of the skew-backs and tangent to the curve of the crown and is represented by the dotted line *DE*.

$$\begin{aligned}
\beta &= 180 - 90 - \alpha \\
&= 180 - 90 - 53^\circ\ 8' \\
&= 36^\circ\ 52' \\
DB &= \frac{DE}{\cos\beta} \\
BE &= DB \sin\beta \\
&= \frac{DE}{\cos\beta}\sin\beta \\
&= DE \tan\beta
\end{aligned}$$

To find the value of *DE* consider a segment of the crown having an arc of one inch. With a radius of 16 feet an arc one inch long would have a subtending chord so nearly one inch long that no appreciable error will be introduced if we assume the chord the same length of the subtended arc.

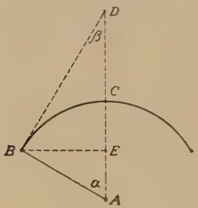

FIG. 4.

The circumference of the crown is $2 \times 16 \times \pi \times 12'' = 1206.4''$.

The volume of segment with 1″ arc is $\frac{1}{1206.4} \times 1058.32 = \frac{1058.32}{1206.4}$ cu. ft.

Brickwork will weigh about 125 pounds per cubic foot. The weight of a segment becomes:

$$\frac{1058.32}{1206.4} \times 125 \text{ pounds} = 109.7 \text{ pounds}$$

The length of the projected area of the crown is $32 \times 12'' = 384''$.

$$DE = 384 \times 109.7 \text{ pounds} = 42124.8 \text{ pounds.}$$

BE represents the horizontal thrust caused by the weight *DE* and equals *DE* tan β or $42{,}124.8 \times \tan 36^\circ\ 52' = 31{,}590$ pounds.

Size of Bands

This stress is taken evenly by two cross-sections of the band at the skew-back if we neglect the static friction of brick on brick.

The stress per cross-section of band becomes one-half of 31,590 pounds or 15,795 pounds.

The joint efficiency will run about 70% so we must provide a band to take $\frac{15{,}795}{.70}$ pounds = 22,564 pounds.

The safe stress in steel using the customary factor of safety of $2^1/_2$ 12,000 pounds per square inch.

$$22{,}564 \div 12{,}000 = 1.897$$

Provide bands with cross-section area of 1.897 square inches.

Value of Brick Friction

One band 10″ x $^3/_{16}$″ gives practically this cross-section area and would take care of the lateral thrust due to the weight of the crown without counting on the static friction of brick on brick.

For the crown to settle, without change in temperature, it would be necessary for the brick at the skew-back to slip on the course beneath, so that a force equal to the weight of the crown multiplied by the coefficient of static friction is available at all times to help support the crown.

Marks gives $f = .6$ to .7 for brick on brick.

Using the lower value of f and neglecting the strength of the mortar joint we have a force of .6 × 132,327 lbs. = 79,396 lbs. This force is more than twice as great as the horizontal thrust of 31,590 pounds due to the weight of the crown. The lateral thrust is taken by the skew-backs and the frictional resistance of brick on brick transmits this thrust to the course directly below and through each course to the foundation of the kiln. Were it not for uneven expanding and contracting no bands would be necessary on a round kiln. Lovejoy states in his "Burning Clay Wares" that, "after the kiln cooled, we found all bands loose, showing that the kiln wall practically carried the crown thrust."

Selection of Bands

The selection of bands becomes a matter of judgment, backed by experience, rather than one for mathematical calculation. By carefully firing the kiln during the first firing and loosening the bands as the heat advances, the thrust due to expansion is largely taken care of. Corrosion of bands due to rust and often to acid fumes while the kiln is cold causes a heavy loss, which must be met. Harrop recommends one $^1/_4$ x 6-inch band at the crown of a 30-foot kiln. Lovejoy says, "we have had $^5/_{16}$ x 6-inch and $^1/_4$ x 10-inch bands burst on smaller kilns than 30 feet in diameter." It is good practice to use two $^1/_2$ x 6-inch bands so that if one breaks the other will hold.

Computations for Kiln Crown Volume

In sector ABE radius = 20′
In sector ACD radius = 20.9167′
In both sectors $\frac{\alpha}{2} = 26° \, 34'$

Substitute these values in formula for volume

$$\begin{array}{ll}
V & = \frac{4}{3}\pi\, r^3 \sin^2 \frac{\alpha}{2} \\
\text{Log } \frac{4}{3}\pi & = .6620896 \\
\text{Log } 20.9167^3 & = 3.9614793 \\
\text{Log } \sin^2 \frac{\alpha}{2} & = \underline{9.3010790 - 10} \\
 & 3.9246479 \\
\text{Anti log } 3.9246479 & = 8407.13 \\
\therefore \text{ Volume } ACD \text{ revolved} & = 8407.13 \text{ cu. ft.} \\
\text{Log } \frac{4}{3}\pi & = .6620896 \\
\text{Log } 20^3 & = 3.9030900 \\
\text{Log } \sin^2 \frac{\alpha}{2} & = \underline{9.3010790 - 10} \\
 & 3.8662586 \\
\text{Anti log } 3.8662586 & = 7349.51 \\
\therefore \text{ Volume } ABE \text{ revolved} & = 7349.51 \text{ cu. ft.}
\end{array}$$

$$8407.13 \text{ cu. ft.} - 7349.51 \text{ cu. ft.} = 1058.62 \text{ cu. ft.}$$

$$\begin{array}{ll}
\therefore\ 1058.62 \text{ cu. ft.} & = \text{volume of kiln crown} \\
\text{Weight of kiln crown} & = 1058.62 \times 125 \text{ pounds} = 132{,}327 \text{ pounds.} \\
\text{Log } 1058.62 & = 3.0247401 \\
\text{Log } 125 & = \underline{2.0969100} \\
 & 5.1216501 \\
\text{Anti log } 5.1216501 & = 132{,}327.
\end{array}$$

Computations of segment weight:

$$\begin{array}{ll}
\text{Log } 1058.32 & = 3.0246170 \\
\text{Log } 1206.4 & = \underline{3.0814913} \\
 & 9.9431257 - 10 \\
\text{Log } 125 & = \underline{2.0969100} \\
 & 2.0400357 \\
\text{Anti log } - 2.0400357 & = 109.743 \\
\therefore \text{ One segment weighs } 109.7 \text{ lbs.} & \\
DE = 384 \times 109.7 \text{ pounds} & = 42124.8 \text{ pounds} \\
\text{Log } 109.7 & = 2.0402066 \\
\text{Log } 384 & = \underline{2.5843312} \\
 & 4.6245378 \\
\quad \text{Anti log } 4.6245378 & = 42124.8 \\
\quad \text{Log } 42124.8 & = 4.6245378 \\
\text{Log tan } 36^\circ\ 52' & = \underline{9.8750102 - 10} \\
 & 4.4995480 \\
\text{Anti log } 4.4995480 & = 31589.9 \\
\therefore\ DE & = 31590 \text{ lbs.}
\end{array}$$

National Clay Works
Mason City, Iowa

A MODERN BRICK PLANT[1]

By J. T. Robson

ABSTRACT

A detailed description is given of the layout and construction of a shale brick plant. This plant fires its ware in a tunnel kiln and is built to conform accordingly.

The Denisons who have been among the foremost brick and tile manufacturers in this country, first started operation of a plant in 1877 at Delaware, Ohio, where they have a brick and tile plant in operation at the present time. It was in 1892 at the Delaware plant, that the 5 x 8 x 12-inch tile, now commonly adopted as a standard size in the United States, was first made.

In 1894 they started a plant, since known as Unit No. 1 of the Ohio Clay Co., at Cleveland, Ohio for the manufacture of brick and hollow ware. This unit has since been in constant operation, although almost continuously improved. Its construction and equipment quite largely follows the usual practice except two chamber continuous kilns and one experimental forced draft periodic kiln. All machinery is electrically driven. This Unit No. 1 produces 45,000 tons per annum of good quality ware at low cost.

In 1895 the standard size 5 x 4 x 12-inch tile was adopted. In 1909 at the Ohio Clay Co., the well-known patented Denison Interlocking Tile was first introduced and in 1913 the manufacture of the perforated or "Cle-Clay" brick (Fig. 1) was begun.

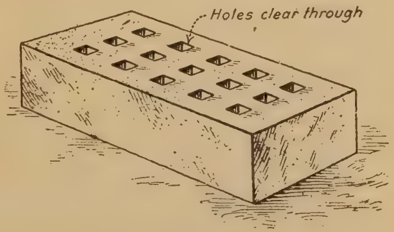

Fig. 1.

In keeping with their progressive attitude, it was quite natural that the Denisons should depart from the old type and fire their product by the better and more modern tunnel kiln method. It was therefore decided to install a tunnel kiln at the Cleveland plant and if satisfactory to make this kiln part of a new unit for manufacturing the "Cle-Clay" brick.

Geo. W. Denison, Vice-President and General Manager of the Ohio Clay Co., who designed this plant, intended to install a tunnel kiln of his own design. He inspected many tunnel kilns throughout the United States and began the designing of one for firing shale brick and building tile. It became apparent to him that the Harrop Car Tunnel Kiln would meet his requirements. This kiln has proven a complete success and made a part of Unit No. 2.

This unit began production July, 1924 and has since been producing

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[1] Recd. Jan. 16, 1925. Presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, Feb., 1925. (Heavy Clay Products Division.)

100 tons per day (7 days per week) of tile or brick of excellent quality with about $^1/_{10}$ of 1% drier loss and less than 1% firing loss. The maximum capacity of this plant is three times the present capacity production and additional kilns and driers are to be added to realize this maximum.

General Layout

In Unit No. 2 the brick move steadily forward from the machine through the drier. They are then transferred to kiln cars. The layout is shown in Fig. 2. This plant is very compact and simple.

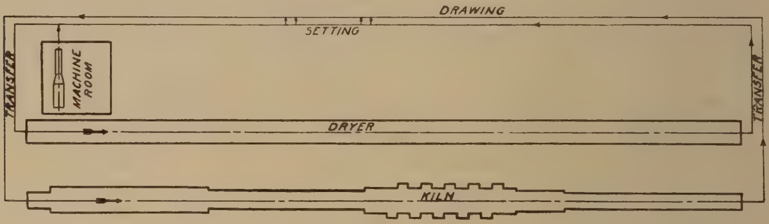

FIG. 2.

Many of its salient features are protected by patents issued and pending, not only the design of some of the equipment used but also the trafficking layout or location of the various units of the plant.

Source of Supply

The material used is Cleveland formation shale, in a bank 120 feet high. The shale is shot down and loaded into approximately 3-yard capacity cars by a Thew electric shovel. The loaded car is hauled by a Plymouth locomotive to the storage pit where the clay is allowed to age. About 300 tons of shale are mined per day. The storage pit will contain 20,000 tons.

Preparation of Material

From the storage pit the shale is transferred to the crusher by a 2-cubic yard capacity clam shell supported on a 112-foot boom. This derrick, together with the crusher house, is shown in Fig. 3.

From the crusher, the shale is belt-conveyed to dry pans and screened through Hummer screens. The screened material is conveyed by a belt 18 inches by 246 feet in length to the storage house. This storage house has a capacity of 200 tons of ground material. It is supported directly above the pug mill by steel I-beam supports.

Machine Room

The ground shale is fed from storage to the pug mill by a disc clay feeder.

The charged drier car is pushed by hand about 30 feet to the three drier tunnels.

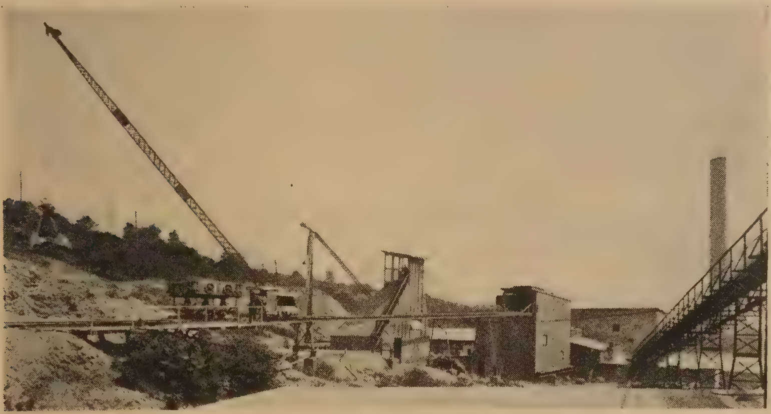

FIG. 3.

Five men are required to operate the machine room—the pug mill operator, three hackers and the transfer man.

Fig. 4 shows the machine room in operation.

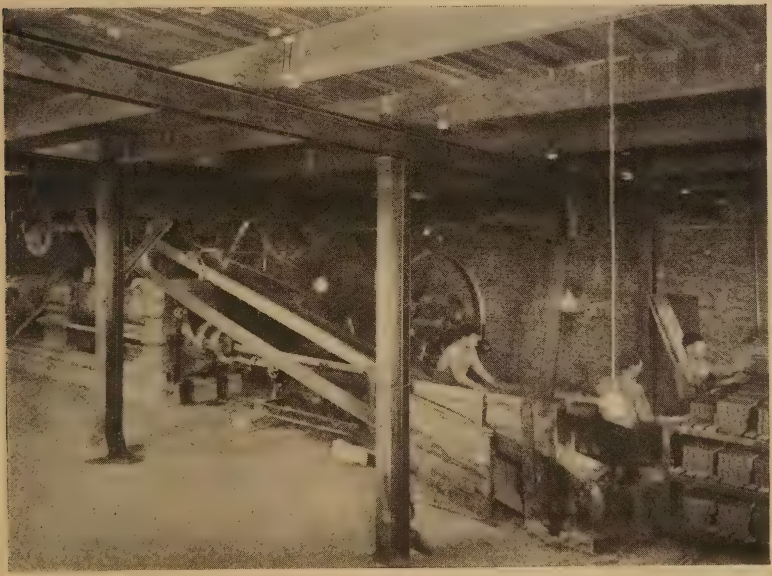

FIG. 4.

Drier

This drier is unique, being designed to fit in with the tunnel kiln. It is located midway between the kiln and the unloading track. It consists of three tunnels each 4 feet wide by $5^1/_2$ feet high and measuring 345 feet in length, almost the same length as the kiln which is 350 feet.

The heat is furnished by an 18-inch flue, which discharges waste directly into each tunnel. The temperature can be regulated by dilution with outside air at the kiln, as described later. An additional source of heat is produced further along in each tunnel by two furnaces each heated with a single oil burner of the W. N. Best low pressure type. The furnaces are located beneath the drier and heat the tunnel by radiation, the products of combustion being drawn off through stacks.

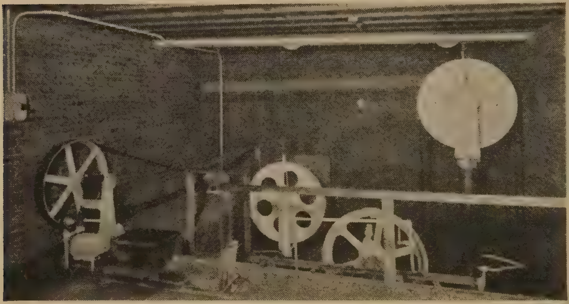

FIG. 5.

The drier is thus in reality a combination of a waste-heat drier and two radiated heat driers in alignment.

The air is drawn down through the tunnel toward the charging end at a high velocity by means of a side discharging fan located in the discharging duct above the tunnels. In this way the green ware comes into contact with air of high humidity, the temperature of which, as it passes down the tunnel, is sustained by means of the furnaces, so that no condensation takes place. The efficiency of this drier is very high, the brick being dried below 2% water content.

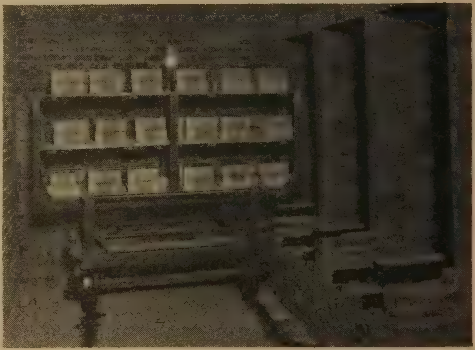

FIG. 6.

Each tunnel holds 44 cars. The cars are pulled through the tunnel by a reciprocating bar extending the entire length of tunnels, to which is fastened lugs which connect with one axle of each car and pull it 7 feet 2 inches. The bar automatically reverses and again pulls the cars forward 7 feet 2 inches, or one car length.

The conveying system is operated by reciprocating hydraulic rams, which are located in a separate room (Fig. 5) beside the discharging end of the drier. At the discharging end of the drier, the cars run onto a transfer car shown in Fig. 8. This is transferred to the return drier track which runs just beside and parallel to the kiln car return track.

Setting of Ware

Each kiln car, 5 feet 11 inches by 6 feet 8 inches, holds more than 2000 bricks. This capacity on each car is made possible by a novel method of setting in piers (Fig 7). There are 7 piers with $3^1/_2$ inch spaces between piers forming flues, which run to the center of the setting into a longitudinal flue about eight inches wide at the bottom. This system of openings of flues allows thorough heat penetration throughout.

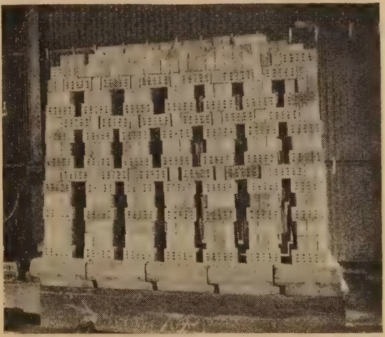

Fig. 7.

The brick are set 17 courses high, the 4-top courses being platted solid. Figure 8 shows the method of setting from the drier cars to the kiln cars. By means of this setting, although the car capacity is very large, the brick are uniformly fired throughout, rendering sorting unnecessary, the entire charge being of No. 1 quality.

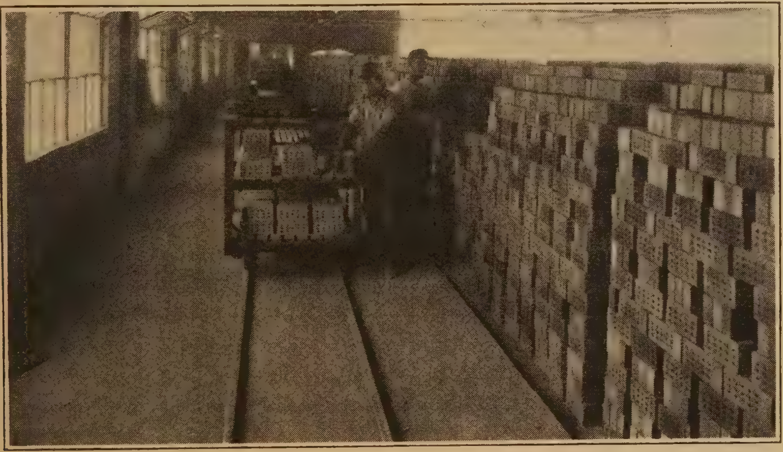

Fig. 8.

Firing

Once every 55 minutes a kiln car is set. The car is pushed by hand into the charging end of the kiln. The whole train is pushed toward the firing zone by means of a 10-ton capacity Ott hydraulic undercar pusher. Inside the kiln, the ram has a lug, which catches the rear of the car and pushes it forward at the rate of one car length, or 6 feet 8 inches, every 45 minutes. Eight minutes are required for the return stroke of the pusher ram.

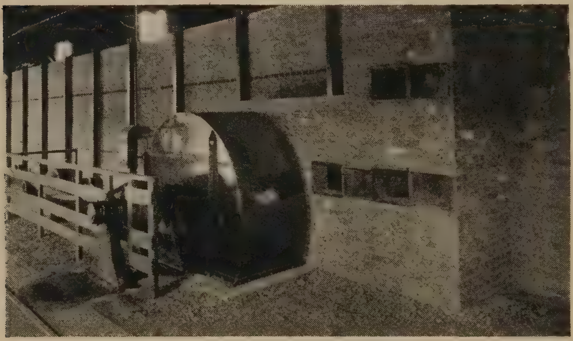

Fig. 9.

As the brick enter the kiln, they come into contact with the warm gases. These gases are drawn down through the kiln chamber proper by means of an exhaust fan and warm air is admitted also through flues above in the crown. This air derives its heat by passing through a double crown over the furnace zone of the kiln. Thus the radiated heat from the crown of the kiln, rather than passing off into the outside atmosphere, is utilized in watersmoking the ware.

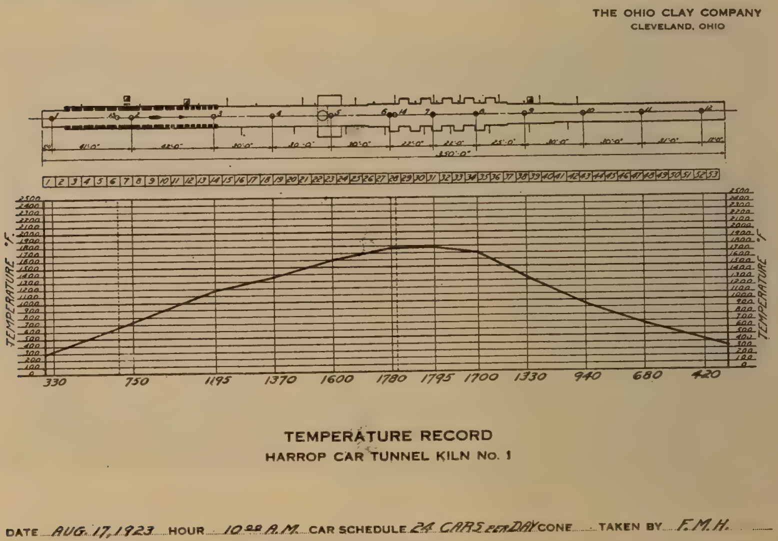

Fig. 10.

The exhaust fan draws the waste gases from the kiln through openings in the kiln side wall and discharges them into the outside atmosphere through a vertical stack 17 feet high. As the ware progresses through the kiln, it gradually heats up according to the temperature record shown in Fig. 10.

Due to the large amount of carbon present, which is common in shales, and also very excessive amount of pyrite or sulphide of iron, it is very essential to maintain thorough oxidizing conditions in the kiln during the heating up or oxidation period to prevent black coring and bloating. The oxidation in this kiln is complete and the color of the fired ware better than that of ware of same material fired in the other kilns.

Shale usually has a vitrification range of about 100° to 150°F between the point of complete vitrification and that of viscosity, or in other words, between that point where the mass is impervious and that where the mass begins to deform or flow. The range of this shale is not more than 20° to 30°, which is exceptionally low. This makes it necessary that the maximum firing temperature be maintained between 1880° to 1900°F with a draft of 0.4 inch, in order to insure sufficient firing and at the same time to avoid overfiring to deformation. The temperature control of this kiln is so easily maintained that unskilled Italian labor successfully operates it.

As the ware passes through the furnace zone, it gradually increases in temperature until it strikes the last or fifth pair of furnaces, where the maximum temperature is attained. Openings on either side of the burners and along the kiln walls allow one to see exactly what is going on in the kiln and the conditions of the ware at all stages of firing.

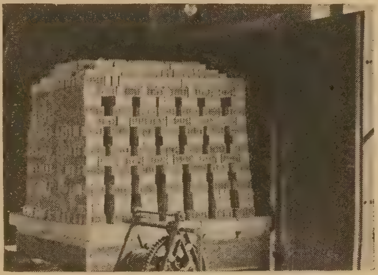

Fig. 11.

The fired ware leaving the furnace zone moves along the tunnel toward the discharging end gradually giving up its heat to the incoming fresh air. Part of this air serves as preheated air for combustion and part is utilized for drying the ware. The excess or waste heat for drying the ware is drawn out through two openings on either side of the kiln into a chamber where it is diluted with the desired amount of outside air furnished through openings in the chamber. The two chambers on each side of the kiln are connected by an 18-inch iron pipe passing over the top of the kiln. From here it is forced by a blower through an underground tunnel, 3 feet 8 inches wide and 3 feet high, to the drier. Figure 9 shows one side of this waste heat system. The three open doors are those which admit outside air for dilution. The inside kiln openings are not visible.

The car reaches the discharge end of the kiln in 48 hours. Figure 11 shows a car of fired ware just taken from the kiln.

Figure 12 shows a view of the cars on the return track just ahead of the pusher. Two car lengths ahead of the truck, cars of green brick ready to be fired can be seen. The brick are unloaded directly into the delivery trucks.

Kiln

The kiln is 350 feet long overall and is located under a building 400 feet long by 32 feet wide. This building is constructed of steel frame work and compound corrugated rust-proof metal. The kiln has a straight-end entrance and a straight-end discharge. It has a placing width of 5 feet 8 inches and a placing height of 5 feet 6 inches. There are 10 direct oil-fired furnaces, 5 alternated on each side. Figure 13 shows the side of the furnace section of the kiln.

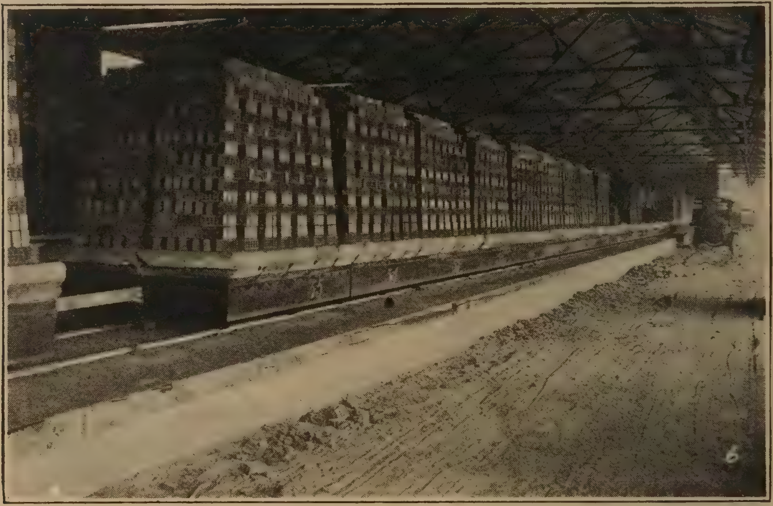

Fig. 12.

The kiln air supply fan is shown in front at the extreme left. The burners are of the W. N. Best oil-firing type.

The fuel oil used is either of the distillate or residual type, either kind proving to be of equal satisfaction. The oil is stored in two 15,000 gallon steel tanks located underground just between the unloading track and drier. From these tanks it is pumped to the burners under 20 pounds pressure. This pressure is supplied by a Viking oil pump, directly connected to a $^1/_4$-h. p. motor.

The oil line contains the necessary valves and strainers. The system is circulatory with the return line emptying into the oil suction line through a pressure relief valve. This avoids unnecessary travel of the oil and unnecessary load on the pumps which would be the condition if the excess oil had to be continuously elevated from the storage tanks. All pieces of equipment and lines in this oil system are in duplicate, so that in case any shutdown is required on the circuit being used, the alternate circuit may be opened and the operation of the burners continued.

Air is fed to the burners under a static pressure of 13 ounces per sq. in. by means of a pressure fan revolving at 3400 r.p.m. driven by a 5-h. p. motor.

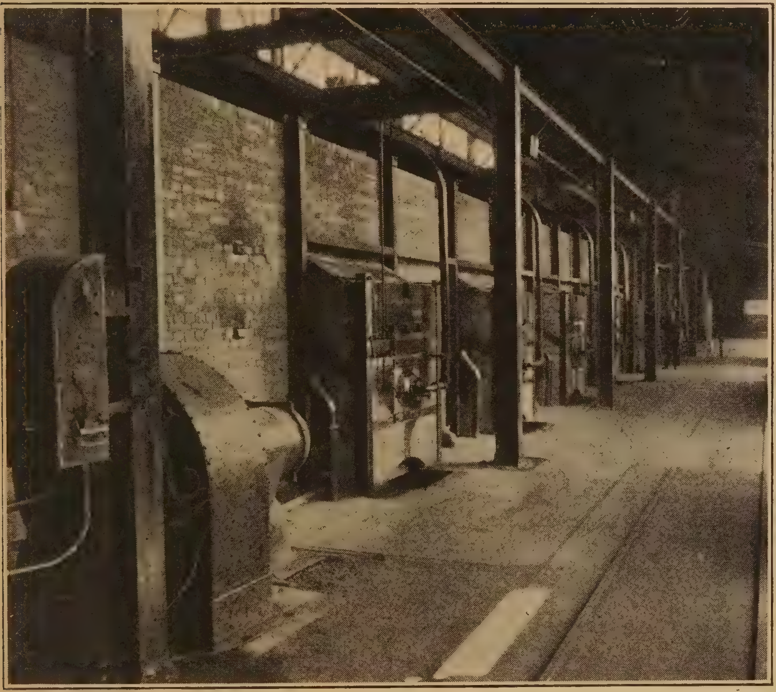

FIG. 13.

An auxiliary steam boiler conducting steam to coils in the bottom of the storage tanks permits heating of the oil to the desired temperature during cold weather. This boiler can be either coal- or oil-fired. This oil system is shown in Fig. 14.

The pyrometer system consists of a Wilson-Maeulen Monopivot Indicator connected with a 30-point switch and a Wilson-Maeulen model C Tapalog, which records the temperature of couples 7 and 8 located in the furnace zone.

Fourteen couples are used. Couples 6, 7 and 8 located in the crown of the furnace zone are of platinum, platinum-rhodium enclosed in double porcelain protection tubes. The other couples which record lower temperatures are of the base metal enclosed in Iralume protection tubes.

Couples 1–12 are located in the top of the kiln extending down 3 inches through the crown. Couple 13 is located in the watersmoking flue and couple 14 is located in the firing zone underneath the cars. Figure 14 shows the location of the pyrometer indicator and recorder on the switch board.

Draft gages on the kiln record the pressure both above and below the cars, so that the actual conditions under which the kiln is operating are known at all times.

Quality of Product

Tests conducted cover the regular physical tests as prescribed in the specifications of the American Society for Testing Materials involving absorption, compression and transverse tests.

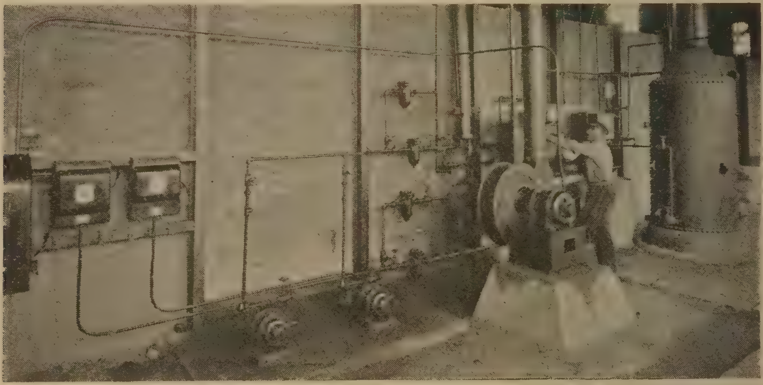

FIG. 14.

In addition special tests[1] were made, such as (1) crushing tests of piers made with brick, using a rich Portland cement mortar, (2) tension tests of the bond of the brick with a rich Portland cement mortar, (3) shear tests of the bond of the brick with a rich Portland cement mortar.

Method of Making Tests The edge compression test and transverse test were made on a 50,000-pound Riehlé Universal Testing Machine. Likewise the tests for bond in tension and shearing were made with the same machine using special fixtures.

The flat brick and pier crushing tests were made on a 200,000-pound Olsen Compression Testing Machine.

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[1] Tests conducted by J. H. Herron Co., Cleveland, Ohio.

Sizes of Brick Used The Cle-Clay brick was approximately 8 x $3^5/_8$ x $2^3/_{16}$ inches. In the following tests and computations, this brick is considered as a solid brick and no allowance is made for the air spaces. The ordinary common clay brick in the same district was larger. The size was approximately $8^1/_2$ x 4 x $2^3/_8$ inches.

Absorption (Average of 5 samples.) The average absorption of the Cle-Clay brick was 10.8% and that of the ordinary brick was 18.5%.

Compression (Average of 5 samples.) In compression, when tested with half brick standing on edge, the Cle-Clay brick broke under a load of 4068 lbs. per sq. in. as compared with 2552 lbs. per sq. in. for the ordinary common brick.

The compression test determined by placing the complete brick on its face gave 7143 lbs. per sq. in. as an average for the Cle-Clay brick and 4542 lbs. per sq. in. for the ordinary brick.

Transverse Strength (Average of 5 samples.) The average modulus of rupture for the Cle-Clay brick was 665 lbs. per sq. in. and for the ordinary brick, 597 lbs. per sq. in.

Compression Tests of Brick Piers Brick piers 16 inches high and 8 inches square were laid up with the brick alternating in successive courses, that is, placing the courses alternately as headers and stretchers. One-half inch mortar joints composed of one part Portland cement and 3 parts of well-graded Pelee Island sand were used.

When 28 days old, the piers were tested in a 200,000 lb. testing machine.

In the piers of Cle-Clay brick, failure occurred first at the mortar joint and then through the center of the brick.

In the piers of ordinary brick, failure occurred first through the center of the brick then at the mortar joint.

When failure occurred through both the brick and mortar, the average load for 3 piers tested was 1200 lbs. per sq. in. for the Cle-Clay brick and for the ordinary brick the average load for 2 piers tested was 750 lbs. per sq. in.

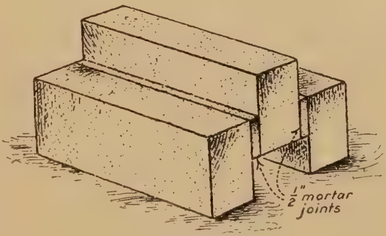

FIG. 15.

Bonding of Brick To Mortar (A.) In tension (3 samples tested). It required an average force of 50.4 lbs. per sq. in. to pull two bricks apart which were held together by a $^1/_2$-inch mortar joint. With ordinary brick the average force required was 15.8 lbs. per sq. in.

(B.) Shearing Test (3 samples tested). These tests were made using 3 bricks laid up as shown in Fig. 15.

An average force of 328.3 lbs. per sq. in. was required in case of the Cle-Clay brick and only 131.3 lbs. per sq. in. for the ordinary brick.

Conclusion

Cle-Clay brick show low absorption, therefore offering a good opportunity for the proper seasoning of the mortar and prevent the necessity of wetting the brick before laying.

Due to its hardness this brick will stand rough handling and dumping. There will be fewer bats and the corners will be in good condition.

They will stand a much better bearing load since they show a stronger unit value in the wall when laid up and subjected to compression.

The perforated brick make a better bond in shear and tension. They therefore possess an advantage in a wall which is subjected to shear such as a retaining wall or in a wall subjected to tension where there is a tendency to overturn.

The entire credit of this plant layout belongs to George W. Denison, sole originator and designer of the many new and unique principles involved in its construction.

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THE MAKING OF DOLOMITE BRICK AND A STUDY OF THEIR PROPERTIES.—II[1]

By A. I. Andrews, G. A. Bole and J. R. Withrow

Investigation of the Squatting of Brick

The squatting of bricks M2–4–4, M2–4–4E, M2–4–4C and M2–4–4M was suspected as being due to the molasses becoming thin when warmed and flowing, thus causing a settling of the brick material. In order to clear up this question, briquettes were made (dry press) 1 x 2 x 4 inches using 2–4–4M composition and molasses in amounts of 10, 15, 20 and 25%. These briquettes were then dried in room conditions and set on end in an electric furnace and heated to 1090°C in eight hours. The briquettes containing only 10% of molasses as a binder, dusted down, thus showing 10% to be insufficient. The other briquettes on removal from the furnace had a faint odor of molasses; they showed no shrinkage or tendency to squat. It may be thus concluded that the flowing of the molasses as the brick becomes warm does not cause squatting.

In a further study of this problem, a standard size brick was made up using 2–4–4M calcine and 20% of molasses as a binder. This brick, on firing to cone 15 down (Fig. 14), showed considerable squatting and shrinkage as was evidenced by bricks M2–4–4, M2–4–4E, M2–4–4C and M2–4–4M previously fired. On examination of brick M2–4–4M microscopically, to determine whether the flux was flowing from the top of the brick to the bottom or not, it was found that no difference could be observed between the material taken from the top or the bottom of the brick. If the flux (glass) which is different microscopically from the mineral constituents, flowed to any considerable extent, its presence in the lower part should be greater than in the upper part of the brick. Further, this brick, 2–4–4M, was broken into two pieces and a specific gravity and porosity determination was made of the top and the bottom parts separately. The following results were obtained:

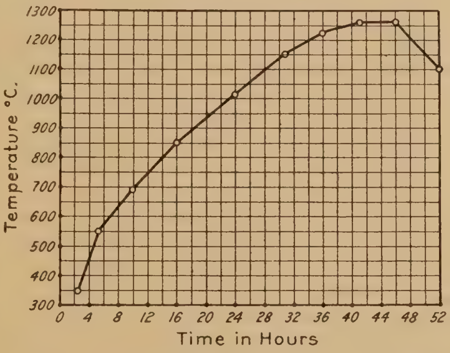

Fig. 14.—Brick firing V. Cone 15 down.

		Density	Porosity
M2–4–4M	upper half	3.11	10.6
M2–4–4M	lower half	3.10	10.7

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[1] For the first part of this paper see *Jour. Amer. Ceram. Soc.*, **8** [2], 84–100 (1925). Presented at the Annual Meeting, Columbus, Ohio,, February, 1925. (Refractories Division.)

Since there is practically no difference in the microscopic appearance, the density or the porosity of the top or bottom halves of brick M2–4–4M, it may be concluded that the squatting is not due to the flux flowing to the bottom of the brick.

As the squatting has been shown to be due neither to the binder, nor to the flow of flux, nor migration of material from top to bottom and that it takes place at temperatures above 1090°C, the only conclusion left is that it must be due to the low viscosity of the melted flux or the lack of adhesion between the flux and dolomite particles. It may be stated here that a small briquette 2–4–4 is very difficult to lift with tongs at temperatures from cone 14 up, due to the ease with which it may be crushed. Furthermore, it is very evident that in dead-burning 2–4–4M, 6–3–6M and 9–0–6M, the 2–4–4M becomes much more vitreous than the others. It is thus concluded that 2–4–4M is very weak at temperatures above cone 14 and that the squatting is due to the weakness of the material and not the binder or any migration of a particular part of the material. A general shrinkage (coalescence) of the weakly bonded brick material fails to act uniformly in all directions due to the friction of the base of the brick with the brick on which it rests. Thus the top contracts (squats) while the bottom remains largely unaffected, adhering to the brick upon which it rests rather than developing sufficient cohesion between its individual particles to draw away. Vertical cracks often develop in the base due to this cause.

Binder Study

Since the three most successful bricks thus far produced show considerable shrinkage, it was decided to attempt to find a binder which would not cause fluxing, thus lowering the refractoriness of the brick. It is suspected that the organic binders cause a reduction of the ferric iron of the flux to ferrous iron, probably in the form of ferrous silicate which is very fusible. The addition of sodium silicate which is very fusible, and is an exceedingly active flux has a great tendency to reduce the refractoriness, especially of a basic material such as dolomite. The following binders were then tried out: water, carbonated water, dry tar, crude tar, bindex, magnesium sulphate.

The preliminary binder study is based on the assumption that if a binder is not satisfactory for small sized bodies, it is not likely to be satisfactory for large bodies such as brick, and second, if the binder is satisfactory for small bodies, it is not necessarily satisfactory for large bodies.

A. Molasses, Dextrin and Sodium Silicate as Binders

In order to determine the limitations and adaptability of molasses, dextrin and sodium silicate as binders, the following tests were made:

Three briquettes, 1 x 2 x 4 inches, were made up (dry press) of each composition and dried very carefully, first at room temperatures and then at 110°C with the exception of those containing molasses which were not subjected to the higher temperatures. The briquettes which dried successfully were then fired, one at cone 14, one at cone 16 and the other at cone 18 down. The porosity and density were then determined by means of the kerosene absorption method previously described.

The compositions used, the percentage binder and the results are shown in the following table:

DRYING AND FIRING RESULTS

Composition	Binder	Per cent binder	Dry	Cone 14 Por.	Cone 14 D.	Cone 16 Por.	Cone 16 D.	Cone 18 Por.	Cone 18 D.	Con.
2–4–4M	Na_2SiO_3	10	Crumb.	...	..	...	..	...	..	NG
2–4–4M	Na_2SiO_3	15	Crumb.	...	..	...	..	...	..	NG
2–4–4M	Dex.	10	Crumb.	...	..	...	..	...	..	NG
2–4–4M	Dex.	15	Weak coarse, and crumbles easily							NG
6–3–6M	Dex.	10	OK	cracked		35.2	3.25	37.6	3.17	NG
6–3–6M	Dex.	15	OK	27.45	2.83	23.95	3.18	20.85	3.22	OK
6–3–6M	Mol.	10	OK	29.00	3.08	10.00	3.03	7.74	3.05	OK
6–3–6M	Mol.	15	OK	swelled						NG
9–0–6M	Mol.	10	OK	41.00	4.02	...	..	26.65	3.26	OK
9–0–6M	Mol.	15	OK	27.3	3.24	26.9	3.08	19.88	3.18	OK
9–0–6M	Na_2SiO_3	10	Crack	...	..	...	..	...	..	NG
9–0–6M	Na_2SiO_3	15	Crack	...	..	...	..	...	..	NG

The sodium silicate binder was a 5% water solution.
The dextrin binder was a one to three mixture of dextrin and water.
The molasses was the same as previously described.

Conclusions

1. Fifteen per cent of the one to three dextrin-water mixture can be used for 6–3–6S composition fired to cones 14, 16, or 18, but cannot be used for 2–4–4M composition under any of the conditions tried.

2. Ten to 15% of molasses can be used for calcine 9–0–6M and 10% molasses can be used for calcined 6–3–6M composition.

3. Fifteen per cent of a 5% sodium silicate solution cannot be used for 9–0–6M or 2–4–4M compositions.

4. From results thus far obtained, it may be stated that molasses can be used for all three compositions, that dextrin can be used for 9–0–6M and 6–3–6M compositions and that sodium silicate can be used for only 6–3–6M composition.

B. Water as a Binder

Water is the logical substance to be used as a binder if such is possible since it is cheap, convenient, and on drying leaves no foreign material to affect the properties of the product.

The following series was designed to show whether or not the ground calcine of any particular mesh size or combination of sizes, possessed sufficient hydraulic properties to permit its being bound into briquettes by water and at the same time not hydrate sufficiently to crack the body. The briquettes (1 x 1 x 4 inches) were made up by tempering the material with water and pressing in a mold by hand. The following table shows the compositions used and the results obtained:

RESULTS USING WATER AS A BINDER

		Mesh (weight grams)						Fired to cone 16	
Comp.	Fines	200	150	100	65	43	Air dry	Porosity	Density
6–3–6M	140	...	...	...	...	...	OK	7.3	2.55
6–3–6M	...	140	...	...	...	...	OK	8.0	2.66
6–3–6M	...	...	140	...	...	...	OK	cracked	
6–3–6M	...	...	...	140	...	...	OK	cracked	
6–3–6M	...	...	...	...	140	...	OK	cracked	
6–3–6M	...	...	...	...	...	140	difficult to take from mold		
9–0–6M	140	...	...	...	...	...	fine cracks	..	..
9–0–6M	...	140	...	...	...	...	base cracked	..	..
9–0–6M	...	...	140	...	...	...	slight cracks	..	..
9–0–6M	...	...	...	140	...	...	cracked	..	..
9–0–6M	...	...	...	...	140	...	OK but weak	..	..
9–0–6M	...	...	...	...	...	140	OK but weak	..	..
2–4–4M	140	...	...	...	...	...	cracked	..	..
2–4–4M	...	140	...	...	...	...	cracked	..	..
2–4–4M	...	...	140	...	...	...	cracked	..	..
2–4–4M	...	...	...	140	...	...	cracked	..	..
2–4–4M	...	...	...	...	140	...	cracked	..	..
2–4–4M	...	...	...	...	...	140	weak	..	..
6–3–6Ma	20	...	20	20	80	...	OK	cracked	
6–3–6Mb	20	...	...	...	...	80	OK	cracked	
6–3–6Mc	10	...	...	...	110	...	OK	15.2	2.40
9–0–6Ma	20	...	20	20	50	30	cracked	..	..
9–0–6Mb	20	...	...	...	100	...	cracked	..	..
9–0–6Mc	10	...	...	...	110	...	OK but weak	..	..
2–4–4Ma	20	...	20	20	40	40	cracked	..	..
2–4–4Mb	20	...	...	...	20	80	cracked	..	..
2–4–4Mc	10	...	...	...	50	60	cracked	..	..
6–3–6M	100	52	...	50	67	...	cracked	..	..

Some of these fired briquettes are shown in Fig. 15.

Conclusions and Remarks

In the above, better results were obtained in drying when the calcined material had stood a short time in the wet condition before molding. This probably is due to the expansion resulting from slaking which goes nearly to completion before the material is pressed into briquettes.

Schurecht[1] noted this same property in his work when aqueous binders were used. It also appears that coarse material is more easily bound than the fines although at first it is very tender and difficult to remove from the mold. This greater ease of binding coarse material may be due to the greater pore space and chance for expansion due to slaking without disrupting the mass, but it is more probably due to the fact that large particles slake much more slowly than the small ones.

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[1] H. G. Schurecht, *loc. cit.*

In conclusion it may be stated that it is not feasible to bind any of the above calcined materials hand molded by means of water alone.

Carbonated Water as a Binder

Since success using water alone as a binder was very limited, an attempt was made to use carbonated water and an atmosphere containing carbon dioxide. In this manner it was hoped that calcium carbonate would be formed with any free lime present preventing it from further slaking by coating the oxide and acting as a binder for the rest of the material until high enough temperature was reached to decompose the calcium carbonate. As with water, briquettes 1 x 1 x 4 inches were pressed by hand, using water saturated with carbon dioxide as the tempering liquid.

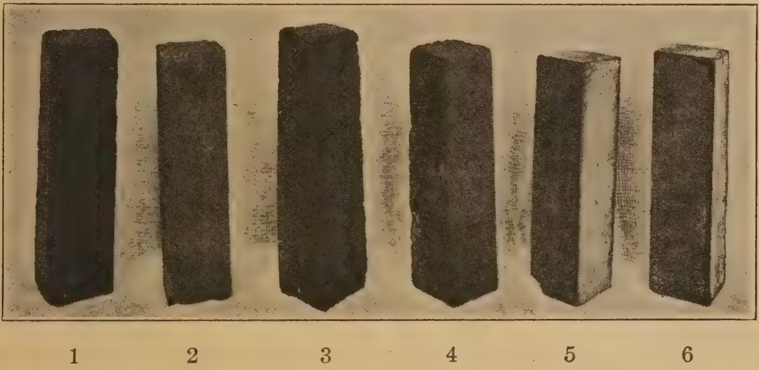

Fig. 15.

The compositions and results of this investigation are shown in the following table:

		Mesh (weight grams)						Fired to cone 16	
Comp.	Fines	200	150	100	65	43	CO_2 dry	Porosity	Density
6–3–6Ma	20	...	20	20	80	...	OK	cracked	..
6–3–6Mb	20	...	..	...	20	80	OK	cracked	..
6–3–6Mc	10	...	..	...	110	..	OK	cracked	..
2–4–4Ma	..	...	20	20	40	40	cracked	..	..
2–4–4Mb	20	...	..	...	20	80	cracked	..	..
2–4–4Mc	10	...	..	...	50	60	OK	16.0	2.42
9–0–6M	130	...	..	...	...	..	OK	cracked	
9–0–6M	...	130	..	...	...	..	OK	cracked	
9–0–6M	...	...	..	...	130	..	OK	18.1	2.30
2–4–4M	130	...	..	...	...	..	OK	..	..
2–4–4M	...	...	..	130	...	..	cracked	..	..
2–4–4M	...	...	..	...	130	..	OK	15.2	2.38

Bindex Bindex is a commercial binder derived from the waste sulphite liquor of the paper mill. As shown in the following table, it was used in solution of 10% and 33% strength, and 15% of this solution was added to the material and was made up (hand mold) into briquettes 1 x 2 x 4 inches in size.

			Firing					
			Cone 15		Cone 17		Cone 19	
Compn. binder	Per cent	Dry	Porosity	Density	Porosity	Density	Porosity	Density
2–4–4M	10	cracked	..	..	..	..	...	..
6–3–6M	10	cracked	..	..	..	..	...	..
9–0–6M	10	cracked	..	..	..	..	...	..
2–4–4M	33	OK	25.3	3.13	13.8	3.20	9.56	3.22
6–3–6M	33	OK	25.9	3.04	15.1	3.16	7.4	3.23
9–0–6M	33	OK	28.8	3.15	21.3	3.25	10.8	3.29

Conclusion Bindex in a 33% solution serves very well as a binder for small briquettes.

Tar Two grades of tar were used in these tests. One was ordinary dry oven tar and the other was crude oven tar. Both of these tars were thin enough at ordinary temperatures to be mixed with the calcined dolomite without heating. The briquettes were made in one-inch cubes, pressed by hand and dried at 110°C for two hours. Five, 10 and 15% of the tar was added and a sample of each composition was fired to cones 15, 17 and 19 down. The results of these tests are shown in the table (p. 184).

Conclusions In all cases 5 to 15% tar seems to serve very well as a binder for small briquettes of 2–4–4M, 6–3–6M and 9–0–6M composition fired to cones 15, 17 and 19 down. They appear to be very strong and well shaped with the exception of those made from 2–4–4M composition which show some squatting.

Conclusions of Binder Study as it Refers to Briquettes

1. Tar serves very well in percentages of 5 to 15% as binder for 2–4–4M, 6–3–6M and 9–0–6M compositions in briquettes.
2. Molasses may be used in making briquettes of 6–3–6M and 9–0–6M composition and brick of 2–4–4M compositions.
3. Dextrin only serves as a binder for 9–0–6M and 6–3–6M compositions.
4. Water is unsatisfactory as a binder for 9–0–6M, 2–4–4M and 6–3–6M compositions.
5. Carbonated water and a drying atmosphere containing carbon dioxide show some promise. Coarse material seems to be preferable to fine.
6. Sodium silicate in amounts up to 1% appears to be insufficient for 9–0–6M and 2–4–4M compositions.

7. These results are only approximate where standard size brick are concerned and it was necessary to carry them further by trying out the most desirable binders on standard size brick.

RESULTS OF THE USE OF BINDEX AND TAR

				Firing					
				Cone 15		Cone 17		Cone 19	
Composition	Binder	Per cent binder	Dry	Porosity	Density	Porosity	Density	Porosity	Density
2–4–4M	Dry tar	5	OK	23.90	3.4	14.3	3.02	..	..
2–4–4M	Dry tar	10	OK	20.7	3.13	4.63	2.14	..	..
2–4–4M	Dry tar	15	OK	7.8	2.98	7.22	2.9	..	..
2–4–4M	Crude tar	5	OK	21.4	3.18	15.6	4.14	2.93	2.97
2–4–4M	Crude tar	10	OK	20.95	3.13	14.05	3.06	1.35	2.99
2–4–4M	Crude tar	15	OK	9.22	3.01	9.64	2.99	1.46	3.10
6–3–6M	Dry tar	5	OK	29.4	3.28	17.1	3.19	6.17	3.02
6–3–6M	Dry tar	10	OK	31.6	3.23	16.7	3.23	6.25	3.04
6–3–6M	Dry tar	15	OK	28.2	3.23	13.8	3.17	4.32	3.07
6–3–6M	Crude tar	5	OK	23.2	3.26	14.1	3.2	5.0	3.04
6–3–6M	Crude tar	10	OK	14.8	3.19	15.1	3.18	4.50	3.08
6–3–6M	Crude tar	15	OK	16.7	3.17	11.7	3.09	4.20	3.07
9–0–6M	Dry tar	5	OK	42.0	3.32	25.6	3.24	11.36	3.16
9–0–6M	Dry tar	10	OK	37.1	3.26	17.4	3.26	8.96	3.11
9–0–6M	Dry tar	15	OK	28.0	3.27	20.7	3.13	7.65	3.03
9–0–6M	Crude tar	5	OK	39.2	3.33	26.1	3.26	9.45	3.20
9–0–6M	Crude tar	10	OK	29.2	3.26	19.6	3.24	11.2	3.17
9–0–6M	Crude tar	15	OK	23.4	3.24	18.0	3.28	5.35	3.93

Carbonated Water and Standard Size Brick

Since carbonated water offered some promise as a binder and would not affect the refractoriness of the body, it was first used in an attempt to make brick from 2–4–4M, 6–3–6M, and 9–0–6M dead-burned compositions. Just sufficient carbonated water was added to make the material withstand removal from the mold. The brick were

RESULTS OF THE USE OF CARBONATED WATER FOR STANDARD SIZE BRICK

		Mesh (weight grams)							
Composition	Fines	200	150	100	65	45	20	H_2O	CO_2 dry
2–4–4M	100	..	200	...	100	2100	..	80	cracked
2–4–4M	...	..	400	410	720	100	950	80	cracked
6–3–6M	200	..	...	...	200	2000	100	90	cracked
6–3–6M	500	..	...	...	...	..	2000	150	OK
6–3–6M	500	..	...	...	...	2000	..	150	cracked
6–3–6M	350	..	50	...	300	1800	..	..	OK
9–0–6M	...	..	200	...	500	1800	..	140	cracked
9–0–6M	400	..	200	100	...	800	1000	90	cracked
9–0–6M	500	..	...	...	...	..	2000	150	cracked
9–0–6M	400	..	...	...	...	2100	..	150	cracked

then placed in a chamber at room temperature into which a slow stream of CO_2 gas was continuously passed. The preceding table shows the screen analysis and composition of the brick made up and the results obtained.

Conclusion These results show that the use of CO_2 in bonding dead-burned dolomite, although it gives a hard and firm body, generally results in cracking when dried.

The brick which are marked OK in the above table cracked on standing in the air for several days. All these brick were then broken up in a mortar and repressed into brick as before with carbonated water and again dried in a CO_2 atmosphere. Again the brick cracked on drying. The surface of the brick was very hard but in spite of the slow drying, the inside of the brick dried slower than the outside and caused cracking. It was then decided to abandon the use of CO_2 as a binder due to the extreme difficulty in drying. However, in order to determine whether a brick could or could not be dried in a humid atmosphere using water as a binder, 6–3–6M was made up of 500 grams of 200-mesh and 3000 grams of 48-mesh residue and tempered with water. This brick was pressed at 500 pounds per square inch and placed in a container over warm water with only an opening to reduce the humidity slightly below 100. This brick crumbled completely and did not appear to be nearly as good as one dried in air. This is likely due to the continued slaking of the dolomite in the humid atmosphere and resulting expansion and disruption. It was then concluded that humidity drying is not practical for dolomite brick due to the hydration of the lime.

Bindex and Tar for Standard Size Brick In order to determine the real value of bindex and tar in the binding of dolomite clinker, these binders were used in making up standard size brick of 2–4–4M, 6–3–6M, and 9–0–6M dead-burned compositions of the following screen analysis.

	Per cent residue		
Mesh	2–4–4M	6–3–6M	9–0–6M
10	0	0	0
20	10.40	12.00	23.31
48	48.00	43.70	30.06
65	15.74	11.86	22.30
100	9.95	8.21	6.01
150	3.97	7.47	3.22
200	8.82	7.47	2.30
Fines	3.12	9.29	12.80
	100.00	100.00	100.00

In making up these brick, 3000 grams of the calcined dolomite were used for each brick.

Brick 2–4–4MB, 9–0–6MB and 6–3–6MB These brick were made by adding 10% of a 33% solution of bindex to the ground clinker, mixing, and molding at 500 pounds per square inch. On drying under room conditions, 6–3–6MB withstood the drying very well but the other two bricks swelled and cracked badly within a few hours. On repressing at 500 pounds per square inch and drying at 110°C in an oven, they swelled and crumbled down completely within thirty minutes. It is likely that this rapid disintegration is due to the acidic character of the bindex accompanied by hydration. It may thus be concluded that bindex cannot be used to bind calcined compositions 2–4–4M or 9–0–6M dead-burned in the form of brick.

The two types of tar used with briquettes (page 184), dry tar and crude tar, were used in making standard size brick. To three kilos of each composition 2–4–4M, 6–3–6M and 9–0–6M, 10% of dry tar was added and to three kilos more of each, 10% crude tar was added. These compositions were then pressed into brick at 500 pounds per square inch after which they were dried for several days, at room temperature, and set very hard and firm.

The following brick were also made up:

Brick M9–0–6ED To the reground material from the unsuccessful brick 9–0–6E, 20% of molasses was added, mixed and pressed into a brick at 500 pounds per square inch. This brick dried well in room conditions.

Brick 6–3–6E CO_2 To the reground material from unsuccessful brick 6–3–6E, a saturated solution of carbon-dioxide was added and it was then repressed into a standard size brick at 500 pounds per square inch. It was dried in an atmosphere containing considerable carbon dioxide. It showed no cracks and was very firm and strong.

Brick 6–3–6M–$MgSO_4$ Schurecht[1] successfully used epsom salts ($MgSO_4$) as a binder for calcined dolomite. The object of which was to form $CaSO_4$ with any free lime present and thus bind the material together. $MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaSO_4$.

To compositions 6–3–6M, 2–4–4M and 9–0–6M 5% of a saturated solution of $MgSO_4$ was added and the batch pressed into brick. These brick, however, cracked on drying. Ten per cent more of the $MgSO_4$ solution was then added and the brick repressed but again the brick cracked on drying. It was thus concluded that $MgSO_4$ could not be used as a binder for the above compositions.

Brick 9–0–6MD In an effort to form brick dry by using dextrin, the ground clinker was wetted with 15% of a one to three dextrin-water mixture and then dried. It was then put in the brick mold and pressed at 500 pounds. On standing for six hours, it showed cracks and later dusted down completely.

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[1] H. G. Schurecht, *loc. cit.*

Brick 9–0–6MS To 3000 grams of 9–0–6M composition, 300 grams of shellac were added and mixed thoroughly. The batch was then pressed at 500 pounds per square inch and dried at room temperatures. At the end of two days it was cracked badly.

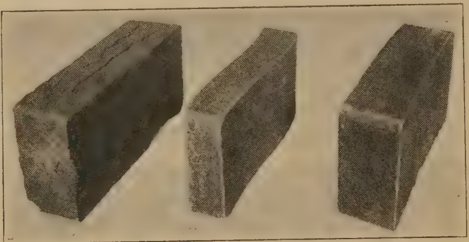
Brick Firing No. 5

Bricks 6–3–6MB, 2–4–4M + 10% dry tar, 2–4–4M + 10% crude tar, 9–0–6M + 10% dry tar, 9–0–6M + 10% crude tar, 6–3–6M + 10% dry tar, 6–3–6 + 10% crude tar, M9–0–6ED, M2–4–4M and 6–3–6ED were included in this firing.

As in previous firings, these brick were set on end on magnesite brick dusted over with 20-mesh magnesite brick grog. The dolomite brick were protected from the direct flame and fired to cone 15 down according to Fig. 14.

Results of Brick Firing No. 5

1. All tar bound brick cracked and fell apart during firings. Fig. 16 shows 2–4–4M + 10% dry tar after firing.



6-3-6MB. 6-3-6E CO_2 2-4-4M

FIG. 16.

2. Brick M9–0–6ED cracked badly.

3. Brick 6–3–6MB cracked and squatted badly (Fig. 16).

4. Brick 6–3–6E CO_2 warped badly, leaning over and fluxing with an adjacent fire brick (Fig. 16).

5. Brick M2–4–4M squatted as has been previously described for this brick.

Conclusions

1. It is not feasible to use 10% tar as a binder for the above clinker.

2. Bindex cannot be used as a binder for clinker of the 2–4–4M or 9–0–6M compositions.

3. Dextrin and molasses together as binders for 9–0–6 compositions are unsatisfactory.

4. The warping and leaning over of brick 6–3–6E CO_2 is likely due to the large amount of Na_2SiO_3 contained.

5. The best binders for dolomite brick thus far used are:

(*a*) 2–4–4M 15% molasses.

(*b*) 6–3–6M 10% of a 5% solution of Na_2SiO_3.

(*c*) 9–0–6M 10% of a one to three dextrin-water mixture.

6. The following binders were not successfully used: bindex, tar, $MgSO_4$, dry dextrin, water, carbonated water and shellac.

Effect of Grain Size on the Rate of Slaking of Calcined Dolomite

Calcined dolomite of the various compositions already mentioned was ground and screened. Samples of about 20 grams were taken from the various sizes and exposed to the room conditions in an open crystallizing dish. These samples were protected from dust by means of a roof and canopy of cheese-cloth. The samples taken and the results of the tests are shown in the following table. Under the heading "mesh," 48 means that the sample passed 20-mesh but was residue on 48-mesh, 100 means through 65-mesh but residue on 100-mesh and 200 means through 150-mesh but residue on 200-mesh.

EFFECT OF GRAIN SIZE ON RATE OF SLAKING OF CALCINED DOLOMITE

			Per cent gain in weight (days)					
Composition	Mesh		1	2	5	9	15	26
2–4–4M	48	8	0.05	0.08	0.18	0.29	0.38	0.48
	100	8	0.06	0.12	0.28	0.87	1.47	2.68
	200	8	0.13	0.26	0.89	1.69	2.47	4.81
2–4–4M3	48	9	0.06	0.12	0.36	0.78	1.11	2.10
	100	9	0.08	0.22	0.70	1.52	2.16	3.18
	200	9	0.21	0.56	1.79	3.67	4.81	6.13
2–4–4M2	48	10	0.06	0.12	0.37	0.76	1.07	1.58
	100	10	0.10	0.27	0.83	1.86	2.56	3.73
	200	10	0.33	0.51	1.59	3.38	4.17	5.94
9–0–6M	48	11	0.01	0.03	0.11	0.19	0.23	0.34
	100	11	0.03	0.08	0.26	0.42	0.57	0.80
	200	11	0.06	0.16	0.47	0.89	1.17	2.00
9–0–6M3	48	12	0.06	0.17	0.50	1.12	1.64	2.51
	100	12	0.12	0.35	0.85	1.78	2.53	3.79
	200	12	0.32	0.87	2.37	5.11	6.69	8.59
9–0–6M2	48	13	0.07	0.19	0.56	1.29	1.87	2.81
	100	13	0.11	0.34	1.12	2.10	2.93	4.33
	200	13	0.36	1.00	2.37	5.69	7.40	7.78
6–3–6M	48	14	0.02	0.07	0.17	0.20	0.39	0.50
	100	14	0.04	0.11	0.30	0.55	0.73	1.00
	200	14	0.09	0.27	0.83	1.48	1.84	2.06
6–3–6M3	48	15	0.03	0.09	0.25	0.44	0.60	0.81
	100	15	0.06	0.16	0.31	0.60	0.84	1.48
	200	15	0.13	0.36	1.07	2.08	3.11	4.08
6–3–6M2	48	16	0.04	0.12	0.33	0.68	0.96	1.43
	100	16	0.10	0.25	0.69	1.59	2.46	3.23
	200	16	0.16	0.45	1.41	2.98	4.03	5.39

From the results as shown by the above table and Figs. 17–25, it may be stated:

1. For a single composition, the smaller the particle the greater the increase in weight on exposure to the atmosphere for a given time.

2. Of the compositions and mesh listed, 150–200 mesh 9–0–6M2 shows the greatest increase in weight in 1, 2, 5, 9, 15 and 26 days while 9-0-6M3 shows very nearly as great.

3. Of the samples used in brick, 2–4–4M shows a decidedly greater tendency to take on weight than 9–0–6M or 6–3–6M, the results on the latter two compositions being nearly equal although 6–3–6M is slightly greater than 9–0–6M.

Conclusions From these results it is concluded that this ground clinker is susceptible to the action of the atmosphere and that any prolonged storage is likely to be deleterious to the material.

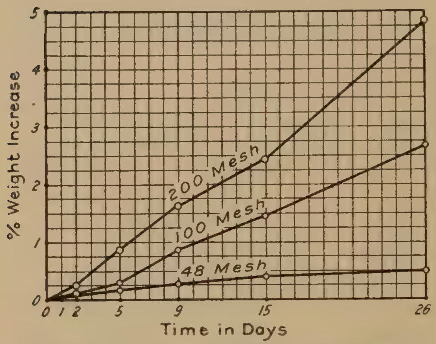


Fig. 17.—2–4–4M. Slaking tendency.

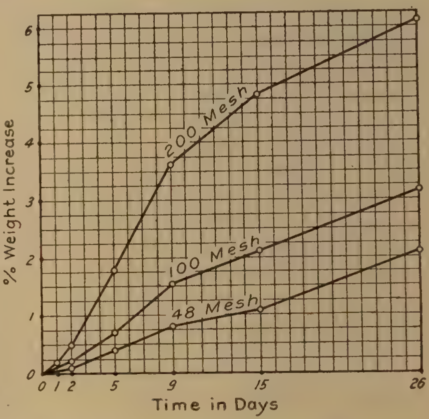


Fig. 18.—2–4–4M3. Slaking tendency.

Fluxing Investigation

In the dead burning of dolomite it is necessary that a refractory be employed with which the dolomite does not react at high temperatures. Neutral or basic refractories have been found to be the best.

Raw dolomite plus flux can be calcined at cone 20 on magnesia brick dusted over with a small amount of magnesia brick grog. If a silica brick is used, a very thick layer of this magnesia brick grog is necessary as the dolomite in calcining rapidly fluxes with the silica until one or the other is entirely destroyed. A kaolin fire brick is also attacked in this manner and the flux becomes even more liquid than in the case of a silica brick. If the layer of magnesia brick grog is thick, however, and the load on it is not too great, the dolomite does not get to the silica or fire clay brick and thus does not flux.

In firing bricks M2–4–4M, S6–3–6M and D9–0–6M on silica brick, the fluxing is very much less than in dead-burning even when carried to a temperature of cone 18. There is, however, a decided reaction resulting in a formation of dust at the point of contact between silica and dolomite.

Chromium oxide is neutral to the dolomite and prevents fluxing. Dolomite may be conveniently fired on chrome brick.

From the above it may be stated that dolomite fluxes energetically with refractories of acidic nature but does not flux with neutral or basic refractories.

Dead-Burning Dolomite

In order to increase the refractoriness of the clinker, an attempt was made to use less flux and heat to a higher temperature than that used by Robson and Withrow.[1] This test consisted in calcining the following compositions made up with water to a plastic condition and pressed into briquettes 1 x 2 x 4 inches by hand: 2–4–4M, 6–3–6M and 9–0–6M using $^1/_2$ and $^2/_3$ of the specified amounts of flux. After firing these briquettes to cone 20, the following tests were made:

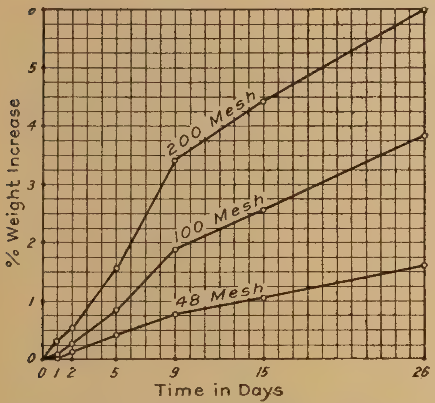


FIG. 19.—2–4–4M2. Slaking tendency.

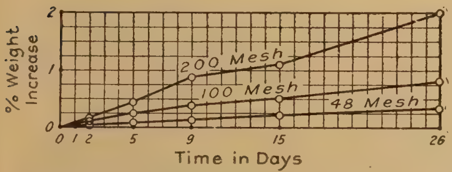


FIG. 20.—9–0–6M. Slaking tendency.

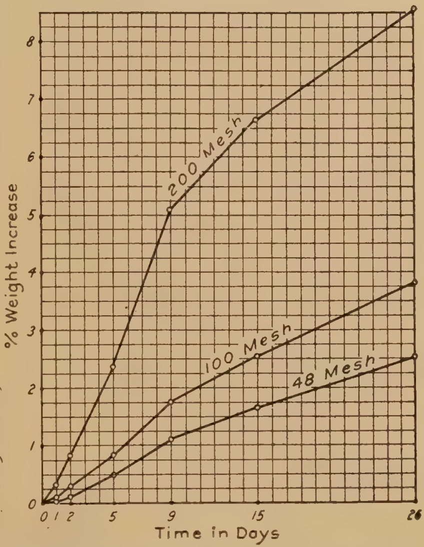


FIG. 21.—9–0–6M3. Slaking tendency.

A. Inside Air Slaking Test Allow the briquettes to remain exposed to the room conditions and note any change in weight or appearance as time goes on.

B. Outside Air Slaking Test Allow the briquettes to remain exposed to the weather (December to April), noting any change in weight or appearance.

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[1] *Loc cit.*

C. Warm Water Slaking Test

Allow the briquettes to rest on a screen in water kept at 75–85°C until they show disintegration.

The following table shows the composition of the various briquettes and the results of the tests just described:

Comp.	Per cent flux	A 4 mo.	B 4 mo.	C Disintegrated,
2–4–4M2	5	no change	no change	1 day
2–4–4M3	7.5	no change	no change	9 "
6–3–6M2	7.5	no change	no change	12 "
6–3–6M3	10.0	no change	cracked 3 mo.	9 "
9–0–6M2	7.5	no change	no change	1 "
9–0–6M3	10.0	no change	no change	1 "

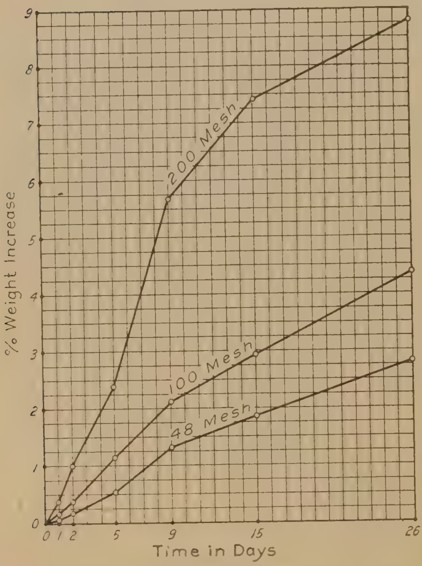

FIG. 22.—9–0–6M2. Slaking tendency.

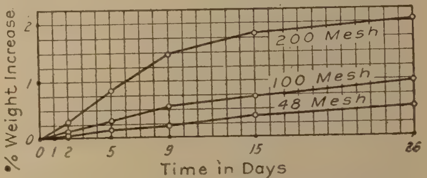

FIG. 23.—6–3–6M. Slaking tendency.

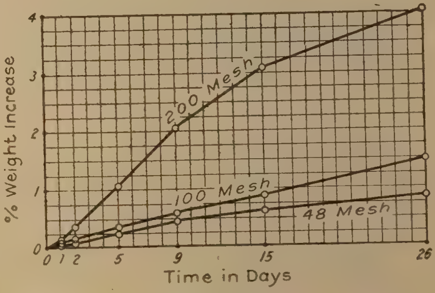

FIG. 24.—6–3–6M3. Slaking tendency.

This shows that less flux can be used if the briquettes are not exposed to severe conditions, but the resistance to slaking is much diminished. See Robson and Withrow.

Since talc is a compound of magnesia and silica, it might easily be suspected of making a good flux for dead-burning dolomite. It was thus tried out in the following experiment:

Maryland and California talc was used in making up briquettes 1 x 2 x 4 inches of 5, 10, 15 and 20% talc with dolomite. These were fired to cone 20 down and subjected to the same tests as the briquettes just described. The briquettes with 20% California talc dusted down on cooling. The others were all hard and firm but, as shown in the following table, they are not very resistant to hydration. The same key is used at the head of the columns as in the table above.

Comp.	Talc.	Per cent talc.	A days	B days	C
TC5	Calif.	5	1	1	1 hr.
TC10	Calif.	10	3	1	1 hr.
TC15	Calif.	15	24	8	1 day
TM5	Md.	5	3	7	1 "
TM10	Md.	10	8	7	1 "
TM20	Md.	20	20	6	1 "

These results show that talc does not satisfactorily act as a flux for dead-burning dolomite under the above conditions.

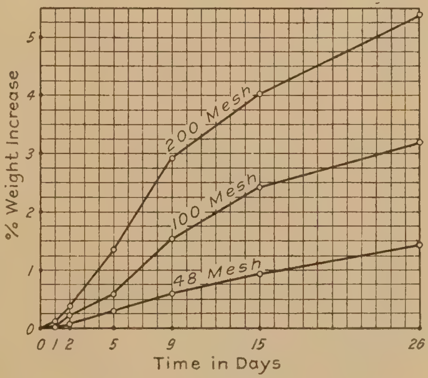

FIG. 25.—6-3-6M2. Slaking tendency.

Cone Fusion Tests

The pure dolomite cones in an Ajax-Northrup induction furnace (Fig. 26) showed a fusion test lower than could be justified; it is believed that the reducing conditions in this furnace were the cause of error. The standard cones in all cases were coated with a grey film which was extremely hard, scratching glass, and which bloated the cones. It is believed that this is a solution of carbon in the cone material which reduces the fusibility of the cones. It is a commonly accepted fact that cone fusions are unreliable in a strongly reducing atmosphere. Since the atmosphere of this furnace is in direct contact with carbon on all sides, it is strongly reducing. Due to this fact and the unreliability of the tests made, another type of furnace was found necessary.

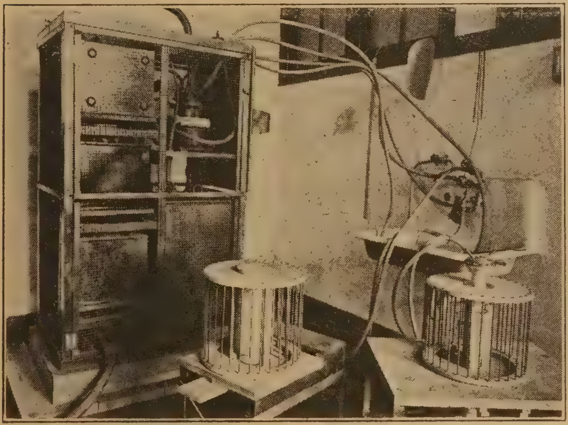

FIG. 26.—Ajax-Northrup induction furnace.

Oxyacetylene Furnace

Since a gas-air furnace does not give the required temperatures and the electric furnaces other than the Ajax-Northrup have the same fault, an oxyacetylene furnace was built. This furnace was built on the principle of that of Wilson.[1]

An iron container, one foot in diameter and 14 inches high was used as the shell. Twenty-mesh magnesia brick grog was used as the refractory material. A dextrin-water binder (1–3) was used to bond the magnesia which was tamped into the shell, leaving a combustion chamber 10 inches deep and $3^1/_2$ inches in diameter. At the base of this vertical chamber were two channels two inches in diameter entering tangentially from opposite sides. Oxyacetylene welding torches were arranged so that the flame caused a spiral motion. At the base of the combustion chamber and in the center was placed a cylinder $1^1/_2$ inches in diameter and 2 inches high on which to place the cone plaque. On this cylinder was placed a layer of chromium oxide to prevent sticking to the plaque. Using the above furnace, the following investigation was carried out:

Cone Plaques

For the standard cones, a highly refractory clay bauxite mixture was used, being made up into plaques and fired to cone 20 down. For the dolomite cones, a plaque was cut out from a magnesia brick.

In order to determine the efficiency and uniformity of the heat in the furnace, a cone plaque containing cones 32 and 33 alternately placed, was put into the furnace and fired. The results were very satisfactory, cone 32 going down before cone 33 in all cases and all cones 32 were down before any of the cones 33 showed distinct deformation.

The following test cones were made up:

1. Raw dolomite, 200-mesh, plus one to three dextrin-water mixture.
2. Dolomite fired to 1100°C 200-mesh, plus dry tar.
3. Dead-burned 2–4–4M composition, 200-mesh, plus molasses.
4. Dead-burned 2–4–4M composition, 200-mesh, plus dry tar.
5. Dead-burned 6–3–6M composition, 200-mesh, plus a 5% sodium silicate solution (about 10%).
6. Dead-burned 9–0–6M composition, 200-mesh, plus dry tar.
7. Dead-burned 9-0-6M composition, 200-mesh, plus one to three dextrin-water mixture.

Results

Test cones 2–4–4M plus molasses, raw dolomite plus dextrin, fired dolomite plus dextrin, 6–3–6M plus sodium silicate, 9–0–6M plus tar and 2–4–4M plus tar, remained standing at cone 38 down. These tests required about an hour, the latter part of the firing being very slow. All these test cones turned black, had sharp edges and great shrinkage. The shrinkage caused some to fall over to an angle of 45° but even these did not lose their shape to a great extent. The standard cones went down naturally being neither discolored nor bloated.

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[1] Hewitt Wilson, "An Oxy-acetylene High Temperature Furnace," *Jour. Amer. Ceram. Soc.*, **4,** 835 (1921).

The above furnace used an excessive amount of gas and since it was desired to reach even higher temperatures, a smaller one was built (Fig. 27). This furnace was 6 inches in diameter, 7 inches high with a combustion chamber $1^1/_2$ inches in diameter and 5 inches deep. The other parts were proportionately smaller with the exception of the cylindrical pedestal on which the cones were placed. The oxyacetylene welding torches used in the large furnace were again used in this small one.

In this latter furnace, the following tests were made at cone 40 down; 6–3–6M plus sodium silicate, 9–0–6M plus one to three dextrin-water mixture and 2–4–4M plus molasses, did not show signs of fusion, having sharp edges and remaining straight with the exception of 9–0–6M which was slightly bent during the early part of the firing. This is believed to be due to shrinkage and was also noted by Robson and Withrow, who attributed it to the formation of a sufficient amount of eutectic or low melting mixture of fluxes present, to take enough dolomite into solution to cause the small tip at the top to lose shape and start bending, but the small amount of flux was presumed to be insufficiently active to cause the entire mass of dolomite to deform.

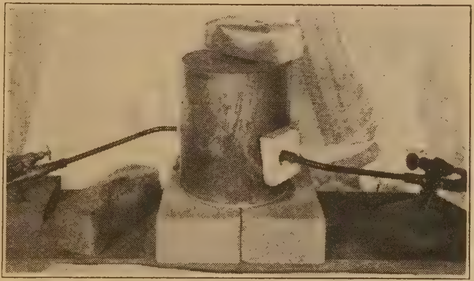

FIG. 27.—Oxyacetylene furnace.

To clear up the reason for the phenomena, just noted, the following microscopic investigation was carried out: cones 6–3–6M, 9–0–6M and 2–4–4M fired to standard cones 20, 28, 30, 38 and 42, were ground to pass 100-mesh screen and then examined under the microscope. 9–0–6M composition shows a distinctly red color, probably due to the high percentage of iron in the flux. It also shows a rapid increase in the amount of isotropic material as the temperature is increased. Since glass is isotropic and most minerals are anisotropic, this may be considered as showing that the fusion is taking place progressively as the temperature increases. 6–3–6M and 2–4–4M compositions do not show this to as pronounced a degree as does 9–0–6M composition.

In heating cones of 9–0–6M composition, it was noted that at comparatively low temperatures, cones 20–26, the cones took about a 2 o'clock position above which no further deformation could be detected. If this deformation was due to a period of glass formation followed by a reformation of minerals, it is likely that the stage of maximum isotropic material would correspond with that of the 2 o'clock position of the cone. Since this is not the case, it is likely that the deformation is due to some other cause, probably due to excessive shrinkage at that particular time. It must, however, be borne in mind that some minerals are isotropic and if such were formed here, the above conclusions would not be correct.

In 9–0–6M composition at cone 42, the material under the microscope has the appearance of many round globules set in a darker matrix. It is suspected that these globules may be crystals going into solution in the matrix which is isotropic. The globules are anisotropic. This would explain the round globules since in solution the corners of the crystal would likely be dissolved first, while if crystals were coming out of the flux, they would have sharp corners. This tends to support the above conclusion that the cessation of deformation is not due to a reformation of crystals since such cannot be detected here.

Results of Cone Fusion Tests

1. The following test cones, 2–4–4M plus molasses, raw dolomite plus dextrin, fired dolomite plus tar, 6–3–6M plus sodium silicate, 9–0–6M plus tar and 2–4–4M plus tar, did not go down when heated to standard cone 38 down in an oxidizing atmosphere.

2. The following test cones, 6–3–6M plus sodium silicate, 9–0–6M plus dextrin and 2–4–4M plus molasses, did not go down at standard cone 40 down in an oxidizing atmosphere.

3. Cone 9–0–6M took about a 2 o'clock position at cones 20–26 and on further heating showed no greater deformation. This is probably due to excessive shrinkage which warps the cone in the early part of the firing.

Spalling and Load Tests

Spalling test on bricks S6–3–6M and D9–0–6M were run. Parallel tests were made on chrome and magnesia brick which had been previously reheated to cone 20 down. The kiln was then heated slowly to a temperature of 1350°C and kept constant at that temperature for one hour. The test brick were then drawn from the wicket and placed on the floor where they were exposed to room temperature. The dolomite brick and the magnesite brick cracked badly for about one-half of their length but the chrome brick did not show any visible change.

It may thus be concluded that dolomite brick like magnesite brick are very susceptible to temperature change and must not be used where exposed to rapid cooling or heating.

The load test was carried out in the usual way using standard brick.

In the furnace used the loading device was in duplicate so that two bricks could be tested at once.

In the tests on dolomite bricks D9–0–6M and S6–3–6M chrome brick was used beneath and above the dolomite brick to prevent fluxing. The tests were made by heating the furnace very slowly with the brick in place to a temperature of about 800°C when the pressure of 25 pounds per square inch was applied and held constant as the temperature slowly rose to 1350°C. (This heating up period consumed 6 hours, $2^1/_2$ hours being required between 800°C and 1350°C.) The brick were kept under the load of 25 pounds per square inch at 1350°C for one hour and then allowed to cool slowly. The ultimate crushing strength could not be determined as a higher temperature could not be attained. On removal from the furnace the brick were measured and the percentage linear contraction calculated.

Results

Brick D9–0–6M shows a linear contraction of 3% and brick S6–3–6M shows a linear contraction of 1.9%. The brick showed no distortion or cracking appearing to have undergone no appreciable change.

This test shows that dolomite bricks D9–0–6M and S6–3–6M are both fairly satisfactory from the standpoint of resistance to load while at elevated temperatures.

Summary and General Conclusions

The conclusions of the various phases of this work may be summarized as follows:

(1) A dead-burning temperature of cone 20 for compositions 9–0–6M (9% Fe_2O_3–0% Al_2O_3–6% SiO_2–85% dolomite 200-mesh), 6–3–6M (6% Fe_2O_3–3% Al_2O_3–6% SiO_2–85% dolomite 200-mesh) and 2–4–4M (2% Fe_2O_3–4% Al_2O_3–4% SiO_2–90% dolomite) is preferable to lower temperatures in that the material is thereby more completely shrunk and can be more easily bonded into brick using aqueous binders.

(2) The use of 2–4–4M composition plus molasses as a binder is unsatisfactory due to the squatting of the brick. This was shown to be inherent in the brick material and not due to a migration of the flux or a softening of the molasses.

(3) Good dolomite brick may be made by calcining 9–0–6M and 6–3–6M composition to cone 20 grinding to pass 20-mesh and making up into brick as follows:

(*a*) 9–0–6M composition plus 13% of a one to three dextrin-water mixture pressed into a brick by hand, dried at room temperatures and fired to cone 18 down.

(*b*) 6–3–6M composition plus 12% of a 5% solution of sodium silicate pressed into a brick at 500 pounds per square inch, dried under room conditions and fired to cone 16 down.

(4) Brick made as described under (3) are hard, firm and well shaped showing little squatting and no cracking.

(5) Some of the properties of these brick may be summarized as follows:

	D9–0–6M	S6–3–6M
Calcination temperature	Cone 20	Cone 20
Binder	Dextrin	Sodium silicate
Firing temperature	Cone 18	Cone 16
Linear shrinkage	7%	9%
Porosity	15.15%	20.33%
Bulk sp. gr.	2.83	2.66

(6) The cone fusion temperatures of the calcines 9–0–6M, 6–3–6M and 2–4–4M are above cone 40 down (2010°C).

(7) In the load test brick D9–0–6M shows a compression of 3.0% and S6–3–6M a compression of 1.9% when exposed to a slowly increasing temperature from 800°C to 1350°C and held one hour at 1350°C under 25 pounds per square inch pressure.

(8) Brick S6–3–6M and brick D9–0–6M when heated on the end face to 1350°C for one hour, like magnesia brick spall badly on exposure to room temperature. This shows that dolomite brick cannot be subjected to sudden temperature change without spalling.

(9) In a study of binders such as molasses, dextrin, sodium silicate, bindex, linseed oil, water, carbonated water, tar and epsom salts, it is concluded that the binders used as under (3) are most satisfactory. Although some success was had with the other binders they are deemed to be of little value for binding calcined dolomite.

(10) The use of talc as a flux is of little value as it does not permanently dead-burn the dolomite. It was also concluded after a careful study that less than the amount of flux used in the above calcines is not satisfactory.

(11) The calcined dolomite compositions studied flux violently with silica and fire brick at cone 16 down but can be safely used in contact with magnesite or chrome brick.

(12) The finer the calcined material is ground, the greater is its tendency to take up weight on exposure to the atmosphere. This is likely due to an increased tendency to slake caused by the greater surface exposed. It is thus evident that this property must not be neglected in the manufacture of brick.

(13) This report shows that dolomite brick of very desirable properties may be made on a laboratory scale and show promise for future development.

(14) The effect of grain size and pressure upon the properties of the brick was realized to be of importance and will be taken up in subsequent studies.

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ORIGINAL PAPERS

SOME FUNDAMENTAL PRINCIPLES GOVERNING THE CORROSION OF A FIRE CLAY REFRACTORY BY A GLASS[1]

By Robert B. Sosman

In requesting a paper on this subject the organizers of the symposium placed no limits on the degree of fundamentality, either upwards or downwards. I am therefore taking the liberty of beginning at the farthest limit of generality that our present knowledge of physical and chemical science permits. It is useful occasionally thus to review the principles upon which permanent progress must be founded, even though no new and striking additions are to be recorded.

Entropy

At the bottom of all the activity we see about us, including among the rest the reactions that take place in a glass-pot or tank, is the principle of *entropy*. Hearers and readers sometimes shy at the word, because it is not a word with which they have become familiar in daily life. But the idea is, in fact, simple. It is only that heat will not, of its own accord, flow up-hill. No furnace-builder ever expects the inside of his furnace to get hotter by the flow of heat inward through the walls from the atmosphere, though there is nothing in the principle of the Conservation of Energy which would make such a happening unlikely.

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[1] Received Feb. 17, 1925. Presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, Feb. 1925. (Joint Meeting of Glass and Refractories Divisions.)

In more general terms, the principle is a statement of the observed fact that the universe as we know it is going full-tilt toward some far-off but invisible dead level. Entropy is the quantitative measure of its downward progress. It might equally well be called "run-down-ness" (Tolman) or "degree of degradation."

Energy

The other great principle underlying our glass-pot reactions is the one incidentally referred to above, that of the Conservation of Energy, according to which an invisible something called *energy* remains constant in amount though continually changing its form of manifestation.

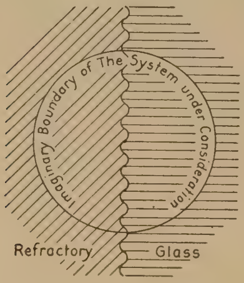

FIG. 1.—Boundary of the system under consideration.

But how apply these principles to the corrosion of a glass-pot? First by setting boundaries to a *system* within which the reactions which interest us are occurring. The system studied may include the whole furnace and pot; or it may be only a tiny volume of material at the boundary of pot and glass, as in Fig. 1. The only limitation to its size is that it shall contain a reasonable number of atoms, say some thousands of millions—its mass would even then be far less than a millionth of a milligram. In the chosen system and the surroundings with which it interacts, taken as a whole, we know there must be a net increase in entropy whenever anything happens.

Zeta

This does not yet enable us to predict very definitely what will happen *within* the imaginary boundary of the chosen system of Fig. 1. Energy may flow in or out across the boundary, and so we must find a quantity involving both energy and entropy, which will tell us what goes on inside. Such a quantity is the *zeta*.[1] So long as any reaction can occur within our chosen system which if it occurred at a constant temperature and pressure would cause a *decrease* in zeta, just so long will things continue to happen in the system. When the possible change in zeta becomes zero, visible changes cease and the system is *in equilibrium*.

Now a refractory which is in equilibrium with a glass at a given temperature will last forever so far as chemical corrosion is concerned, obviously a very desirable state of affairs, especially in a glass tank. The study of the conditions and the values of zeta which lead to equilibrium is therefore of the first importance.

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[1] Called by G. N. Lewis the "free energy" and by other writers a "thermodynamic potential." So important a quantity should have a short and easily remembered name, however, hence I propose to use *zeta*, the name of the Greek letter which J. Willard Gibbs, who laid the foundations of chemical thermodynamics, employed to represent the quantity.

The picture I am trying to present is that of a ceaseless striving after equilibrium at every point where equilibrium has not already been attained. If the refractory in Fig. 1 is not in equilibrium with the glass, then changes leading toward equilibrium are going to take place in both refractory and glass. The case is not essentially different from that of the cup of coffee which we had for breakfast. A cup of hot coffee with a spoonful of sugar in the bottom is a system which is not in equilibrium. The dissolving of the sugar is a process accompanied by a decrease in the zeta of the system. Hence the sugar immediately begins to dissolve.

It may fairly be asked at this point whether we have gained anything by thus restating the case. Why not say simply that sugar is soluble in water? If we expected never to be interested in any other case then there would be no gain in using what seems a more abstruse form of statement. But there are hundreds of ceramic reactions in which we are all interested, each of which would be a single unrelated problem if considered in the obvious way as a case of specific solubility of A in B, but which will fit together into a systematic body of facts from which many further deductions can be drawn, so soon as we regard them from the more general standpoint of the dependence of reactions upon zeta.

Phases and Their Properties

Let us look more closely into the details of the system shown in Fig. 1. We find that it consists of several *phases*, each of which is homogeneous, so far as the microscope can discern. There is a liquid phase, the molten glass. There are also two or more crystalline phases formed from the material of the refractory.

Each of these phases has a set of characteristic properties, by which it may be recognized, no matter where or in what masses it may be found. Among these characteristic properties are the entropy per gram, the energy per gram, and consequently the zeta per gram. We cannot know with exactness the *absolute* values of these properties, but we can know very precisely their *differences* from one substance or condition to another, and these differences are all we really need, just as in measuring temperature we arbitrarily select a zero and proceed to measure the departures from that zero.

A convenient assumption for entropy and energy is to call their values for each chemical element zero at 0°C and 1 atmosphere pressure. This fixes the values of entropy, energy and zeta for every substance at every temperature and pressure, for we need to know only the heat-changes in passing from the chemical elements over to any specified compound or mixture under any specified conditions.

This will indicate the great importance to ceramics of a knowledge of specific heats and heat-changes (heats of reaction, heats of formation, heats of fusion). Their importance is far beyond their practical usefulness in calculations on ceramic processes, for fuel is used so inefficiently—I speak now from the standpoint of physics and chemistry, not engineering—in the firing of ceramic products, that we might guess at the specific heat or assume that all specific heats are the same, with accuracy enough for many practical purposes. The real usefulness of accurate heat data is in giving us general values for zeta. Once supplied with a good set of tables of zeta for various substances used in ceramics, we would have the data with which to answer many a question which can now be answered only after expensive practical trials.

The Third Law

Though it is a little aside from my principal theme, I should like, in passing, to remark upon the importance to ceramic science of a new law of entropy which some have considered important enough to call the "Third Law of Thermodynamics." It states that the entropy-change at the absolute zero of temperature is zero in an isothermal process involving only solids (and possibly liquids.) This principle, which has been demonstrated by means of measurements extending down to within 20° of absolute zero, makes it possible to integrate curves of specific heats ranging up from very low temperatures, and to obtain values of zeta up to very high temperatures with a minimum of high-temperature experimentation. Science thus offers the paradoxical spectacle of an investigator using liquid hydrogen and liquid air to determine constants for use in kilns and blast-furnaces, a thing obviously absurd to the nontechnical man, as absurd as the notion that yellow fever can be eliminated by devoting one's time to killing mosquitoes. And yet, as everyone knows, the Panama Canal was dug with fly-swatters and oil-cans, after the unaided steam-shovel had failed.

The Phase Rule

Data on the zetas of many elements and inorganic compounds have already been assembled, but the ceramic oxides and compounds are lagging behind in this regard. Meanwhile, we must look out for another important—indeed necessary—set of facts which must precede the determining of zeta. I refer to the identification of the possible phases which can occur in the system under consideration. These facts, together with others which might be calculated from the zeta tables if we had them complete, are usually assembled into the *phase-rule diagram* of the system of substances with which we are concerned.

The same principle of decreasing zeta which has already been referred to also enables us to predict with certainty the number of phases which can be in equilibrium under given conditions, when we know the number of chemical components of which the system is made. This important generalization is the *Phase Rule.*

Application to the Alumina-Silica Refractory

Let us assume for convenience of discussion that the refractory consists essentially of alumina and silica, in about the proportion of one formula-weight of Al_2O_3 to two of SiO_2. Originally in the form of a colloidal, suspended, or finely divided hydrous silicate such as kaolinite, the substance of the refractory has been dried and fired, so that it has already started on its way toward the state of equilibrium corresponding to the temperature of the kiln or the furnace. What that state of equilibrium is may be seen from the phase-rule diagram worked out by Bowen and Greig, and presented before this SOCIETY a year ago.[1] (See Fig. 2.)

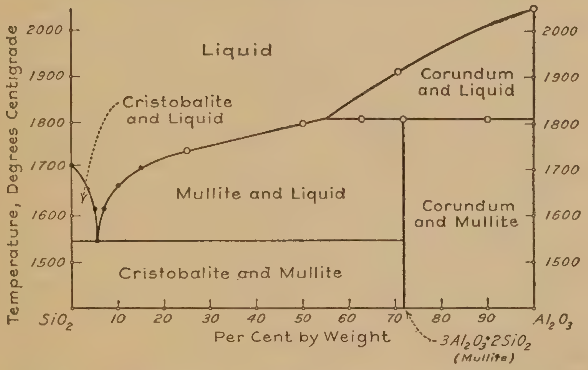

FIG. 2.—Temperature-concentration diagram of the chemical system $SiO_2||Al_2O_3$, according to Bowen and Greig. Weight percentages.

The Phase Rule tells us that $P + F = C + 2$. P is the number of phases, F is the number of arbitrarily determinable variables, and C is the number of components. Since the compositions of the phases in this system can be completely described in terms of the two oxides, SiO_2 and Al_2O_3, the number of components, C, is 2. Therefore $P + F = 4$.

What are the conditions determining P and F in the wall of a glass tank? In the first place, we are working under the constant pressure of one atmosphere, which arbitrarily fixes the value of one variable. The temperature also is constant, at say 1350°C, which fixes another variable. The number of phases in equilibrium, then, can be 2, but not more.

Figures 2 and 3 show what these two phases may be. (Figure 3 has been recalculated to molecular percentages from Fig. 2, which is the diagram by Bowen and Greig.) Pure dehydrated kaolinite contains alumina and silica in the proportion 1:2, represented in Fig. 3 by the line *RR*. The final state of equilibrium of the wall at 1350° is therefore represented by the point *W*. It will be a crystalline mixture of tridymite, which is the stable form of pure silica at 1350°, and mullite, which is a compound of the formula $3Al_2O_3.2SiO_2$. There will be no liquid present and no other compound, provided nothing but SiO_2 and Al_2O_3 are present in the refractory.

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[1] N. L. Bowen and J. W. Greig, "The System: Al_2O_3–SiO_2," *Jour. Amer. Ceram. Soc.*, **7** [4], 238–254 (1924).

The Glass

Let us assume for definiteness of discussion that the glass is an ordinary soda-lime glass of the molecular composition $Na_2O:CaO:6SiO_2$. This is an example of a 3-component system, hence $P + F = 5$. If, as before, the pressure is set at 1 atmosphere and the temperature at 1350°C, there may be 3 phases in equilibrium but not more.

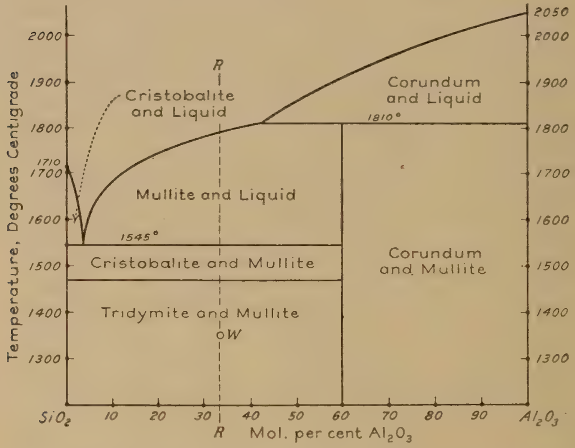

FIG. 3.—Temperature-concentration diagram of the chemical system $SiO_2||Al_2O_3$, with concentration expressed in molecular percentages.

No complete investigation of this chemical system has been made, but some information is available on the siliceous side of it, which is the one in which we are interested. The phase-rule diagram of the system $SiO_2||Na_2SiO_3$ has just been published,[1] and that of $SiO_2||CaO$ has been fairly well known for some time.[2] From the form of these two diagrams it is highly probable that the state of equilibrium for the mixture $Na_2O:CaO:6SiO_2$ at 1350° is a single liquid phase, the molten glass, with no crystalline phases. This is also rendered highly probable, though not necessarily proved, by the fact that it is feasible in practice to manufacture the glass at this temperature.

The System of Refractory and Glass

Consider again the system represented in Fig. 1, consisting of a small portion of glass and a small portion of tank wall, inclosed within an imaginary sphere whose position is indicated by the circle in the figure. We have to deal now with a four-component chemical system, the system $SiO_2||Al_2O_3||CaO||Na_2O$. Unfortunately its phase-rule diagram is known only in the most fragmentary way, but some general statements can be made, nevertheless.

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[1] G. W. Morey and N. L. Bowen, "The Binary System Sodium Metasilicate-Silica," *J. Phys. Chem.*, **28,** 1167–1179 (1924).

[2] G. A. Rankin and F. E. Wright, "The Ternary System $CaO–Al_2O_3–SiO_2$," *Amer. J. Sci.*, **39,** 1–79 (1915).

$P + F$ is now equal to 6. At the arbitrary pressure and temperature already adopted, the value of P may therefore be 4, that is, four phases can coexist in equilibrium, if no arbitrary limitation is set on the composition of the phases. Since it is unlikely that there will be two immiscible liquid silicates containing all three of the basic oxides, the four phases, if so many are present, will probably consist of one liquid (molten glass) and three crystalline phases.

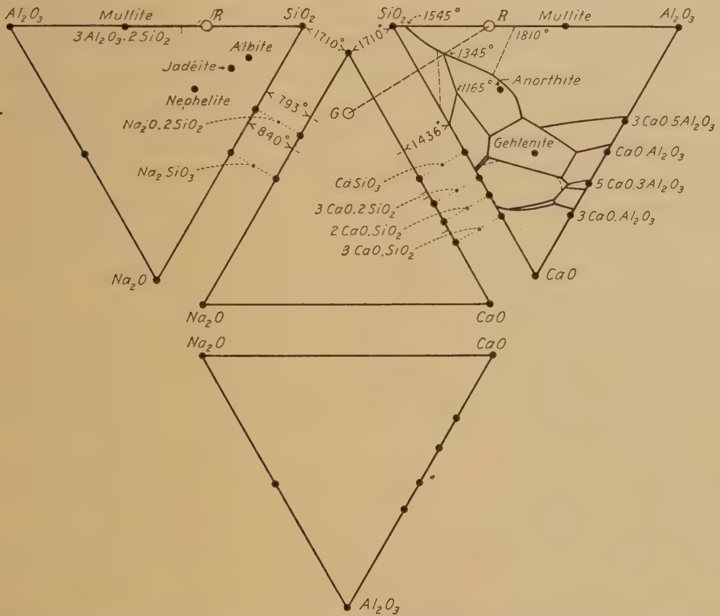

FIG. 4.—Outline of compositions in the four 3-component systems which bound the 4-component system $SiO_2||Al_2O_3||CaO||Na_2O$.

Graphical representation of equilibrium diagrams becomes more difficult as the number of components increases. With two components, we could get along with a plane diagram as in Figs. 2 and 3. With three components, we can represent all possible compositions by the now familiar plane triangular diagram, leaving the third dimension perpendicular to the plane to represent temperature or pressure. When we have four components, all possible compositions can be represented by points within an equilateral tetrahedron in space, but no coördinates remain in which to represent temperature or pressure. We are then driven to the procedure of using a series of tetrahedrons, each representing compositions at one temperature and pressure.

The four faces of the tetrahedron still serve to represent the compositions in the four three-component systems which can be made from four components. They are outlined in Fig. 4 for the system $SiO_2||Al_2O_3||CaO||Na_2O$. The composition of the glass is represented by the point *G*, that of the refractory by *R*, and compositions produced by the mixing of the two would lie along a line within the tetrahedron, extending from *G* to *R*.

As already noted, the state of equilibrium for a three-component mixture of the composition $Na_2O:CaO:6SiO_2$ at 1350° is probably that of a single liquid phase, the molten glass. Experience with aluminous glasses indicates, further, that at least a small percentage of Al_2O_3 can be dissolved in this glass without its being brought thereby into equilibrium with a crystalline phase containing one or more of the four oxides.

The juxtaposition of a molten glass of the composition $Na_2O:CaO:6SiO_2$ and a refractory of the composition $Al_2O_3:2SiO_2$, as in Fig. 1, therefore produces a system which is not in equilibrium. The alumina-bearing crystalline phase of the refractory, mullite, must therefore immediately begin to dissolve.

Whether tridymite also must dissolve to bring the system to equilibrium it is not possible on this general basis to foretell. Experience shows, however, that silica, as well as alumina, is dissolved from the refractory, and the presumption is that this reaction, also, is one leading towards equilibrium.

Thus there is produced a liquid phase whose composition lies within the tetrahedron, on or near the line *RG*.

The ultimate state of equilibrium of the imaginary system represented by Fig. 1 cannot be predicted exactly, both because we lack the necessary phase-rule data, and also because we have not defined just how much glass and refractory the arbitrary boundary incloses. Possibly, at 1350° the whole would become liquid. Or it might be that before the portion of refractory included within Fig. 1 was completely dissolved, new crystalline phases would appear. Phases which might possibly result from attainment of equilibrium at 1350° within the boundaries of Fig. 1 are: (1) aluminous liquid glass, (2) alumina (corundum), (3) mullite ($3Al_2O_3.2SiO_2$), (4) tridymite (SiO_2), (5) sodium disilicate ($Na_2O.2SiO_2$), (6) pseudowollastonite ($CaSiO_3$), or (7) a lime-soda feldspar in the series between albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$). Not more than four of these could exist together, and the aluminous glass would almost certainly be one of the four. At all events, equilibrium would ultimately be reached and visible changes within the system of Fig. 1 would cease.

In actual fact, changes never quite cease, for the boundaries of this system are wholly arbitrary. To the right of the figure, particularly, is a mass of glass which is very large compared with the mass of Fig. 1, and this glass is no longer in equilibrium with the glass inside Fig. 1, whose composition has been changed by the reaction with the refractory. Diffusion must therefore occur across the boundary of the figure, into the pot or tank of glass, even though there should be no mixing by convection, and since this upsets the equilibrium within Fig. 1, further reaction must occur between the glass and the crystalline phases.

Nevertheless, the imaginary closed system of Fig. 1 is to a limited extent realized in practice, because of the slowness of diffusion and convection. If the phases which are the natural product of the reactions within this system can be provided beforehand in manufacturing the refractory, equilibrium at the boundary will be by that much nearer to attainment and corrosion should be correspondingly reduced. It ought to be possible to select more intelligently a refractory for a particular temperature and a particular glass, when detailed data on the stable phases and the values of zeta in such a system as $SiO_2 || Al_2O_3 || CaO || Na_2O$ shall have become available.

Rate Versus Equilibrium

If I seem to have devoted a considerable share of my time to the statement of these fundamental principles without bringing forward the data necessary for a detailed and quantitative application of them, it is because I wish to emphasize the distinction between the idea of equilibrium and another even more important idea, that of the *rate of reaction*. The distinction might appear so obvious as to require no emphasizing, were it not for the fact that authors of articles and discussions so often fail to keep the distinction clear. The possibility of confusion is shown by the very fact that we often use the same word for both ideas. We speak of the "solubility" of sodium chloride in water, for instance, meaning the concentration of the saturated solution *in equilibrium* with the salt, while we speak of the "solubility" of quartz in hydrofluoric acid of various strengths, meaning in this case the *reaction-rate* of the quartz with the acid.

An understanding of the equilibrium toward which reactions are moving must come first. There cannot be a race without a goal. But the race itself may be a long and complicated proceeding, and some of its features must next be considered.

Rates of Reaction

The principles governing rates of reaction are not so well understood as those governing equilibrium. Some of the phenomena of reaction-rates appear to have no rhyme or reason whatever, but the proportion of such is gradually being reduced by the progress of experiment and theory.

We know with certainty that the occurrence or non-occurrence of a reaction depends upon whether or not the zeta-change associated with the reaction is a *decrease* (page 192). It appears also logically necessary that the magnitude of the zeta-change should be related in some way to the rate, but the form of the relation is not known. We do know that they are not proportional, for some reactions with a large zeta-change go very slowly, while others with a small zeta-change go rapidly. The same contrast is found in many mechanical systems.

A piece of wet clay, for instance, can be deformed by the pressure of a finger, while the green brick made from it will stand a fairly heavy load without deforming. Although the force is so much greater in the latter case, the rate of response to it is practically nothing, because the absence of water so greatly increases the frictional resistance to motion of the particles.

In spite of the lack of quantitative data, we can find certain qualitative principles which will apply to the case of the glass and the refractory.

Diffusion

A fact of basic importance is that reactions between atoms or between molecules can only occur when they approach within distances of the same order of magnitude as their own size. There is no evidence to show that a given atom has any attracting or repelling effect upon a second atom which is so far away that hundreds or thousands of others intervene. If they meet, it is by virtue of their own wanderlust.

It is this wanderlust of atoms, families of atoms (molecules), and even tribes of atoms, that we usually call by the name *diffusion*. It is obviously a very important quantity when we are dealing, as in the present case, with a reaction at the boundary between a solid and a liquid. If the alumina and silica which enter the boundary zone from the refractory, and the lime and soda which enter from the main mass of glass, all diffuse very slowly, then equilibrium will soon be very closely approached in the zone of liquid glass next to the refractory, and activity will accordingly nearly cease, if the liquid is not carried away from the surface mechanically.

Surface Reaction-Speed

A second important factor in the rate of reaction between solid and liquid is the actual speed of combination between atoms at the active surface. The high temperature in the glass tank leads us to expect that this speed will be very great, for speeds of reaction are sometimes more than doubled by an increase of temperature of only 10°. On the other hand the slow rate at which silica and the siliceous alkali feldspars change from the crystalline to the amorphous state suggests caution in making assumptions about speeds of interaction of siliceous phases even at high temperatures. But, on the whole, it appears likely that the speed of interaction at the surface is enough greater than the speed at which the products diffuse, that diffusion will be the controlling factor. The slower the rate of diffusion, the slower the rate of attack by the glass.

Factors in Speed of Diffusion

The next question, then, is: What controls the speed of diffusion?

Most important of all is the nature of the medium through which diffusion occurs. It is most rapid in gases. In liquids it is immensely slower, while in solids it is several hundred times slower still and is usually not measurable at all at ordinary temperatures. Bowen[1] has shown that the rate of inter-diffusion of silicates of the character typified by diopside ($CaSiO_3 . MgSiO_3$) and albite-anorthite mixtures ($NaAlSi_3O_8$ and $CaAl_2Si_2O_8$) at 1500°C is of the same order of magnitude as the rate of diffusion of glycerin in propyl alcohol at room temperature.

In liquids of similar character and at the same temperature, the rate at which a given substance diffuses is inversely proportional to the *viscosity*. Now the viscosity of a glass increases rapidly with its silica content. The dissolving of silica from the refractory produces a more siliceous glass near the surface of contact, and therefore strongly depresses the rate of diffusion, thereby diminishing the rate of attack.

There is one kind of diffusion which deserves to be considered here because it is so much more rapid than the usual slow diffusion through a liquid medium. I refer to phenomena such as the passage of hydrogen and helium through vitreous silica (quartz glass) at a high temperature. This may become so rapid as to take on the character of an actual flow of gas, as if through capillary pores, yet it is not a flow of this kind, as is shown by its failure to agree with the laws based upon kinetic theory.

There is some evidence that rapid diffusion such as this may take place through a molten glass. It is perhaps encouraged by the presence of halogen compounds, water, and in general those substances which the petrologist calls "mineralizers" and to which he assigns an important role in the formation of crystalline silicates in a molten magma. If such diffusion does occur, it is not a matter of indifference to the refractory manufacturer what fining agents the glass-maker adds to his glass, even though they are minute in amount and cannot be shown to have any direct chemical action on the refractory. These considerations are still hypothetical, however, and must not be taken as a statement of fact established experimentally under glass-manufacturing conditions.

Mechanical Factors

Mention should be made of the mechanical factors in the rate of corrosion, though these are more difficult to define in general terms than the physico-chemical factors. The first is the factor of flow or circulation in the glass. In the considerations which have preceded, we have assumed, for simplicity, that the liquid glass stands still. This is never true. There is convection due to differences of density and to the movements of gas bubbles, and in the tank there is progressive flow forward. These movements of the glass come to the aid of diffusion by carrying away or mixing the glass near the walls, thus making the concentration gradient steeper and increasing the rate of diffusion.

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[1] N. L. Bowen, "Diffusion in Silicate Melts," *J. Geol.*, **29**, 295–317 (1921).

Although I do not know of any study which has been made of the character of flow in a glass tank, it may be worth while to distinguish two logically different cases, namely, steady flow and turbulent flow. Steady flow is the type which takes place through a smooth straight pipe or out of a properly designed orifice or nozzle. Turbulent flow is the more usual kind, occurring in a rough pipe which has sharp bends.

Steady flow yields a uniform and predictable gradient of pressures in the stream, and correspondingly a uniform concentration gradient which produces a minimum of disturbance in the natural or stationary rate of diffusion. Turbulent flow, on the contrary, produces thorough mixing and gives the maximum aid to diffusion, thereby increasing the corrosion.

Viscosity is the important factor in determining the character of flow. The greater the viscosity, the slower the response to whatever forces are causing circulation

This has a secondary consequence, also, in controlling the amount of turbulent flow, because the steady type can be converted into the turbulent by an increase of speed.

For these two mechanical reasons, then, high viscosity in the glass next to the wall is desirable: first, it decreases the speed of flow of whatever kind, and second, it reduces the proportion of turbulence.

The direction of circulation of the glass in a small, uniformly heated pot, as shown experimentally by Coad-Pryor,[1] depends upon whether the density of the original glass is raised or lowered by the initial attack on the wall. In a tank, on the contrary, it is reasonable to suppose that this factor is of smaller importance, and that the differences of density which cause circulation are due principally to the cooling of the glass at the walls.

Another mechanical factor is the texture of the refractory. A porous refractory, which permits the liquid to penetrate and attack the bonding material between the grains, would appear logically to be less resistant to corrosion than a dense refractory which offers a much smaller surface for interaction between the liquid glass and the solid phases. This factor has often been emphasized in discussions of pot and tank corrosion. The point has been brought out that rapid but *uniform* corrosion may be preferable to corrosion which is slow but which produces stones with such material as is set free from the refractory. This is a consideration of very different kind from those which form the basis of the present paper.

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[1] E. A. Coad-Pryor, "Notes on Pot Attack," *J. Soc. Glass Tech.*, **2**, 285–287 (1918).

Summary

Emphasis is placed on the important distinction between *equilibrium* and *rate of reaction*. The occurrence of any reaction is determined by the value of the quantitative property called *zeta*, which can be found by means of measurements of latent and specific heats. This quantity also determines the number of phases present at equilibrium and the way in which the equilibrium changes with temperature. The number and the character of these phases depend upon the composition of the chemical system made up of glass and refractory; the problem in the corrosion of a pot or tank by a lime-soda glass, for example, is a problem of the crystalline phases in equilibrium at a certain temperature with an aluminous liquid phase in the four-component system $SiO_2||Al_2O_3||CaO||Na_2O$.

The rate at which progress is made toward the attainment of this equilibrium is determined mainly by the rate of *diffusion*, which in turn depends upon the viscosity of the liquid glass. Mechanical factors, such as steady or turbulent flow, must also be considered.

Geophysical Laboratory
Carnegie Institution of Washington

Discussion

Albert B. Peck: Frankly, I do not feel that I am enough of a physical chemist or that my experience with glass has been sufficient to entitle me to make any detailed criticism or discussion of Dr. Sosman's excellent presentation of the principles involved. But I do feel that occasion should be taken again to call to the attention of refractory and glass manufacturers the fact that much of the data accumulated by members of the staff of the Geophysical Laboratory can be made of great use in practical manufacture. Most of the information cannot be taken over bodily because the manufacturer is limited in many ways, especially with regard to the purity of materials used, because of which crystalline phases may appear at points other than where they appear when pure materials are used. This does not mean, however, that the fundamental principles involved cannot be used to advantage in many cases.

Dr. Sosman's mention of mineralizers under which are included dissolved halogens, water, boron compounds, and others, as an aid to diffusion in glass is common knowledge to the mineralogist, but I wonder how many glass manufacturers have thought of it in that way. As I said in the beginning, I am not very familiar with glass, but if my memory is right in this matter, halogen compounds, especially fluorides, are an important constituent of many opal glasses and I think Dr. Washburn has obtained SiF_4 from opal glass by his special method of evacuating the furnace while the glass is molten. Also as I recall it, opal glasses are very fluid glasses, and are not easy on pots or tank walls. If this is true it seems worth while to give some consideration to the relation of these mineralizers and diffusion.

Dr. Sosman also mentions the matter of the texture of the refractory, referring especially to its porosity. There is another point regarding texture. I once had occasion to examine microscopically a pot wall for the effect of the glass upon it. The body was one which had a coarse grog with a fine binder. The corrosion had been decidedly uneven and the microscopic thin section showed very plainly that the glass had rapidly penetrated into the areas of the fine binder. At some points it was apparent that two such tongues of glass had nearly met behind a good sized grog particle and in a short time a stone would have been thrown off as a result. Stones themselves are not desirable but the further point is that if that body had been more uniform in texture it might have lasted longer.

Another suggestion which may be away from the point is that the most successful pot or tank block would seem to be what may be termed a one component body. It may not be composed of one crystalline compound alone, but should have a very large percentage of that compound. With this would need to be combined a great resistance to solution. Careful study would show what would be a satisfactory compound in regard to the latter factor. How to form that compound or a body carrying a high percentage of it, into a pot or tank block might prove to be a large order but it probably will be done sometime just as many things which once seemed impossible are common now.

PRESENT AND FUTURE WALLS FOR USE AGAINST MOLTEN GLASS[1]

By Robert J. Montgomery

ABSTRACT

The early glass pot was made of German clay, which, because of its lack of refractoriness, was later mixed with Missouri fire clay. The war made it necessary to substitute American bond clay for the German which was still used. The batch drifted from one of high silica, such as that obtained with all German clay, to one of comparatively low silica without its being realized. While German clay is now available, it is recognized to be unnecessary.

Aside from going back to a high silica pot and the use of porcelain pots for special glasses, little progress has been made in pot composition. The pot of the future will probably be of clay, but of white firing clays, carefully selected. The structure will be uniform, rather fine grained with greater refractoriness, depending upon greater freedom from impurities. Its chemical composition will be suited to the composition of the glass melted and the temperature of the furnace. The density will be under control and will depend upon the fluidity of the glass at the temperature of melting.

Introduction

Way back in 1910 at Ohio State, Prof. Purdy gave me a clay in the senior laboratory to identify for some commercial use. It was a refractory clay of some description and among other tests, I made a small pot and melted some cullet in it. Apparently there was little or no attack of the glass on the clay so I reported that the sample was a glass pot clay. Although I was very much in doubt at the time, I am now convinced that my conclusion was correct. A clay which may be formed into a pot and will not be readily attacked by molten glass is a glass pot clay.

While the subject of this paper could be taken to include both glass pots and tank blocks, the data and experience used for this discussion is based largely on glass pots. I believe the fundamental principles involved are the same for both.

History

H. L. Dixon has very well outlined the early history of the present pot.[2] First it was German clay, which, when used alone, starts to overfire between cones 15 and 20 and fuses at cones 27 to 28.

A more refractory batch was required and the Missouri fire clay came into its own, being mixed with the German clay. This fire clay is more refractory than the German clay. At cone 20 it shows but little overfire and has a fusion point of cone 32.

Soon after this the World War started and the importation of German clay was cut off. There was a grand scramble for substitutes and it was

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[1] Recd. Dec. 22, 1924. Presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, February, 1925. (Glass and Refractories Divisions.)

[2] *Bull. Amer. Ceram. Soc.*, **3** [11], 416 (1924).

this period, 1914 to 1918, that forced a lot of progressive work on the subject. As early as 1912 some of the pot manufacturers were working on the German clay substitute so no very serious interference with production resulted when the foreign supply was cut off. Much to the surprise of many of the old timers, business went on about the same as usual.

Two new pots were introduced, one the high silica batch by C. H. Kerr, then of the Pittsburgh Plate Glass Co., and the other the porcelain pot by A. V. Bleininger, then of the Bureau of Standards. After the war a reaction set in and there has been a considerable demand for German clay, although many pot manufacturers are still using their new batches.

The slowness of the development of the glass pot industry has been largely due to three things:

(1) The pot is sort of a side issue from the main project of manufacturing glass and very few glass house superintendents go beyond insisting upon good pots in the most general of terms. This is true whether the pot house is at the glass plant or not.

(2) The time required to experiment with batches is very long. It has often been the practice not to use pots under a year in age, although this is now cut to as low as three months. At best it takes an average of six months to get the clay from the pit to the furnace and with a furnace life of one month to a year as in the case of a tank block, very few changes can be made in a period of two or three years. Furnace conditions so often make results of tests doubtful and unless there is a decided failure, it is difficult to draw conclusions.

(3) The cost of the clay and labor is small compared to the value of the glass which may be spoiled if a manufacturer finds himself with a lot of pots on hand which seemed good during an experimental period but which fail to give good results when introduced into regular operation. Glass manufacturers are very slow in taking up anything new in pot composition as so much is at stake.

Present Status

There are four types of glass pots on the market:

1. German clay blended with American clay
2. American clays blended. No German clay
3. American clays blended, high silica batch
4. Porcelain type using American clays.

Good pots have been made of all of these types, which brings out the significant fact that all refractory clays are glass pot clays and that my laboratory report, calling an unknown fire clay a glass pot clay back in 1910 was correct. The highly plastic German bond clay is a glass pot clay and the flint fire clay, raw or fired, which has little or no plasticity, is a glass pot clay. It is not the individual clays used, but the properties of the blended combinations, which are important.

Raw Materials A study of the American and English specifications for glass house refractories[1] shows how hopeless a task it is to classify the properties of glass resisting refractories in terms of softening points, porosity, shrinkage, etc. In general terms the American specification calls for cone 29 as the minimum for any clay used and the English specification calls for cone 28 to 29 for Grade 3 bond clay. The Gross Almerode clay will hardly pass cone 28. I have tested samples giving about cone $27^1/_2$. One thing is apparent and that is, specifications cannot be written which will bar any refractory clay which is reasonably free from impurities such as iron, 2.5% Fe_2O_3 being the maximum given by the English specification. As a matter of fact it is not the individual clays which are subjected to operating conditions but it is the mixture of raw materials so compounded as to give a batch which has the desired properties. In other words, in picking out raw materials its effect upon the batch should be studied more than its characteristics when studied by itself.

A case in point is the use of substitutes for German clay. Attempts were made to find an exact duplicate in an American clay. It is now known for a fact that the need of German clay was more mental than actual and by proper blending of American clays, satisfactory results in the finished batch can be obtained.

It is fairly well understood that a glass pot clay should be of the refractory type, having a fusion point of cone 29 or above, although some of the German clays and German clay substitutes have a fusion point as low as cone 27. The kaolins, flint clays and ball clays used should show no tendency to overfire at cone 20 while the bond clays, whether German or American, usually show considerable bloating at cone 20 but none at cone 15. The fire clay may or may not show overfire at cone 20, but in case it does it should be very slight.

The chemical properties are not so definite except as they show the typical difference between the various clays. The kaolin will have a high alumina and low silica content, as 38% Al_2O_3 and 46% SiO_2 with the iron content as low as 0.5%. This will grade to a sandy clay like the Gross Almerode with 71 to 73% SiO_2, 15 to 19% Al_2O_3, with iron at 1.5%. In some of the fire clays and impure ball clays the iron will run as high as 2.5%.

Proportioning the Pot Batch Little need be said on the physical properties of the pot up to the time it goes to the furnace. The pot manufacturer has learned to so proportion his raw clay and grog to give the desired plasticity, drying shrinkage and strength in the green state. From 40 to 50% raw clay is used, the balance being non-plastic material. Of the raw clay 8 to 12% is generally a good bond clay firing to a dense body at a low temperature and having a long vitrification range. The balance of the raw clay portion is made up of fire clay or kaolin. This is where the Missouri fire clays have been largely used. Flint clay is seldom, if ever, used raw. It has no plasticity, so it is only of value as a grog, which should be ground fine to avoid causing stones.

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[1] *Bull. Amer. Ceram. Soc.*, **2** [3], 29 (1923); *Jour. Soc. Glass Tech.*, **3,** 4 (1919).

The non-plastic portion or 50 to 60%, may include pot shell, feldspar, silica, alumina, whiteware bisque, calcined flint clay and fired fire clay, pot shell usually being about 10 to 25% of the total batch when this material is available.

More exact proportions cannot be laid down because much depends upon the properties of each clay used and the properties desired in the pot. Papers by Clark and Forsyth,[1] Grafton,[2] Brownlee and Gorton,[3] give a very good idea of the care necessary to make a good pot after it is proportioned.

The result of all the foregoing is a pot in good physical condition delivered to the glass plant for use. It will stand heating up in a rather crude pot arch to an uncertain temperature, can be transferred to a melting furnace without cracking, will stand up in the furnace and give reasonably good results when melting soda-lime or low lead glass at normal melting temperatures.

Resistance to Destruction

Whether it be tank block or glass pot, from this point on we are no longer interested in the plasticity and bonding power of the clay, the coarseness of the batch to allow drying, arching and transferring to the furnace or the heating of a tank furnace. What we have is a wall for use against molten glass at melting temperatures. If we want to study this wall as it is in service we must look to the pot shell or broken up pot or block after it comes from the furnace.

Composition Analyses of pot shell are not very plentiful in ceramic literature and apparently it is not considered to be of importance. The work by Bleininger[4] on optical glass pots, and Fuller[5] on pot mixtures, does not give any information on glass pot composition as far as the per cents of the various oxides go. Still, the Pittsburgh Plate Glass Co. has taken out two patents (1,217,953 and 1,278,164) calling for the addition of 8 to 30% free silica as sand to the batch, and English[6] after testing a mixture of 90% natural sillimanite with 10% ball clay states that his figures conclusively prove that glasses attack a well-fired clay crucible much more rapidly than they attack a similar crucible made from sillimanite mixture.

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[1] *Jour. Amer. Ceram. Soc.,* **5,** 146 (1922).

[2] *Ibid.,* **3,** 653 (1920).

[3] *Ibid.,* **4,** 97 (1921).

[4] *Ibid.,* **1,** 25 (1918).

[5] *Ibid.,* **3,** 569 (1920).

[6] *Jour. Soc. Glass Tech.,* **7,** 248 (1923).

I am listing thirteen analyses showing a silica content from 56.45% to 78.6% and an alumina content from 16.9% to 38.8%. It is possible to get practically any working properties desired, any shrinkage and porosity of the pot shell combined with the necessary refractoriness and use approximately the limits here given.

TABLE I

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO-CaO	Alkali
1	56.45	38.83	1.39	1.56	0.74	1.28
2	60.86	35.40	1.09	....	.54	2.02
3	62.60	33.00	3.02	0.41	.87	0.46
4	62.71	32.85	2.95	....	.51	1.00
5	63.80	33.25	1.74	....	.10	1.17
6	64.17	31.46	1.86	....	trace	2.51
7	66.68	29.12	1.55	1.10	0.77	0.75
8	66.92	28.71	0.94	....	.72	2.59
9	69.53	26.65	.81	....	.48	2.53
10	70.37	26.92	.91	....	.42	1.16
11	75.50	21.64	1.80	....	.48	0.65
12	77.00	19.90	1.72	1.05	.53	.46
13	78.60	16.90	0.70	2.2	.90	.50

Numbers 1, 3, 4, 5, 6, 7, and 11, are pots made by five of the best known pot firms in the country. Numbers 2, 8, 9, and 10 are of the porcelain type, as may be guessed by the rather high alkali content. Number 12 is a foreign pot. Number 13 is Gross Almerode clay with the combined water left out, as given by Fuller in his study of bond clays.[1]

According to our best knowledge, there was a time in this country when Gross Almerode clay comprised the entire pot, part being fired and the remainder raw clay. I have therefore listed the analysis of this clay with the other pot batches and we find that it is a very high silica batch. Evidently a high silica batch is not new. When the German clay content of the batch was cut down, the batches drifted to ones of lower silica content probably because the Missouri fire clays used had a lower silica content.

In three analyses given by Evers[2] (see Table II) pots used in 1868 and 1887 are compared with the 1921 pot. There is a 5% lowering of the silica content with a corresponding increase in alumina. Evers recognizes this as a definite change but is not sure that it is an improvement.

A glance at the eutectic curve between silica and alumina shows that any proportion of these two materials will be refractory enough to withstand glass melting temperatures if pure raw materials are used. The eutectic point of 94.5% silica will fuse at 1545°C or 2813°F.[1] With 70% to 80% silica in the batch, the melting point would be at least 100°F above this. It would seem foolish to say that the ultimate composition is not important.

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[1] *Jour. Amer. Ceram. Soc.*, **4**, 904 (1921).

[2] *Jour. Soc Glass Tech.*, **5** [20], 331 (1921).

Table II[2]

	1868	1887	1921
SiO_2	71.1	70.0	65.3
Al_2O_3	25.0	24.5	28.5
Fe_2O_3	2.0	2.0	2.2
TiO_2	1.1	1.1	1.1
MgO-CaO	0.5	0.7	0.7
Alkali	.8	1.2	1.4
	100.5	99.5	99.2

Structure Next comes the structure. In use, a pot is very porous as it comes from the arch and has a water absorption of about 30%, almost porous enough for a water filter. After two or three days in the furnace it reaches more or less an equilibrium, that is, little more change will take place in the pot, due to the temperature of operation. The fluxes have melted and combined, the reactions between alumina, silica, alkali, iron, lime, etc., have gone nearly to completion, as nearly as can be, hindered as it is by the size of grain of the material.

We still have a porous mass. The degree of density will depend upon the composition of the batch and the temperature to which it is exposed. The porosity of a pot, after going eleven melts, showed 13.6% at the rim and 21.7% at the center of the bottom. A pot of the same composition after twenty-seven melts showed 5.5% porosity at the extreme edge of the rim and 24.0% at the center of the bottom.

Table III shows how the density of the shell can be controlled by increasing the amount of flux in the batch and by that means decreasing the amount of open pore space and still maintain the necessary refractoriness.

Table III

Percent porosity	Fire clay pot		Porcelain pot	
	1	2	1	2
Rim	9.28	13.70	2.61	1.13
Belt	10.92	18.25	2.39	1.85
Knuckle	14.21	13.99	1.82	1.82
Bottom	17.45	19.08	6.37	3.52

It is undoubtedly true that heavy lead glass of better quality can be made in a pot of low porosity like the porcelain one given above than in the old porous fire clay pot, disregarding any ordinary difference in the ultimate analysis.

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[1] Bowen and Greig, *Jour. Amer. Ceram. Soc.*, **7,** 243 (1924).

[2] Analyses given by Evers calculated to the fired basis.

Firing The effect of firing a rather refractory porcelain pot for six hours at 2600°F before filling in is shown below (Table IV).

TABLE IV

Position	Per cent porosity
Rim	5.55
Belt	5.90
Knuckle	5.83
Bottom	5.85

In this case all parts of the pot would be equally resistant to penetration.

We see that it is possible to make a pot of the required refractoriness with a variation in absorption or porosity from about 2% up to 25% and maintain almost any silica-alumina ratio desired. The present day pots are within the limits as indicated, although I believe that in most cases the properties obtained are more or less accidental and are not deliberately controlled by the pot manufacturer.

The Pot of the Future

Glass manufacturing is changing. The melting temperature is higher and the variety of glasses made increases every day. The pot has not changed to any extent since the Missouri clay replaced a large portion of German clay. The porcelain pot is not used outside of a few plants making special glasses and, as now made, it is not suited to general purpose needs.

Several new raw materials for pots have been suggested but it is not likely that any material will replace clay for some time to come. The clay pot can be improved and that is the problem now before the pot maker and glass maker alike.

As far as I can see, there are only two important things to consider when the clay wall comes in contact with the molten glass at furnace temperature. First is the chemical composition of the wall and second is the physical structure. When these two points are determined for a given glass and melting temperature, the body must be so compounded that the batch may be worked into a pot or block and successfully brought to furnace temperature.

Influence of the Glass But all glasses are not alike and all furnaces are not run at the same temperature, so it is not at all likely that all glass can be melted in the same pot. There is no reason to believe that a high silica pot will be best for soda lime glass, lead glass, opal glass, colored glass, etc., or that a high alumina pot is best for all. The problem then, is to classify glasses not only as to composition but as to furnace temperature and to establish the best silica-alumina ratio for each class, having the physical structure of the clay body under control at the same time. If the density of the pot is not considered in conjunction with the chemical composition, the work would be of little value.

A very fluid barium glass will penetrate a pot with a porosity of 20% almost like water penetrates a sponge. There is no need for the glass to attack the pot. The glass will run through it.

This extreme case illustrates the point. The corrosiveness of a glass depends largely upon its fluidity or viscosity. A pot wall which is penetrated by the glass does not last long.

Prefiring It has often been suggested that prefiring the pot to a high temperature before use would give the desired density. While this is certainly true, considerable could be done in proportioning the pot batch so it would mature at the normal furnace temperature, giving the desired density.

Pure Pot Materials Pure kaolins, china clays, ball clays, and flint clays low in iron, should make up the batch and the fluxes used should be added with direct intent. There is no reason why alkali should be the only flux used to control the bond. Some other fluxes might be found to fill up the holes in the skeleton kaolinite body, which would resist the chemical action and penetration of the glass far more than an alkali. The fire clays now used introduce a heterogeneous flux of impurities under no control. Herbert Insley, in his study of glass refractories,[1] has given us considerable to think about on the subject of the flux. A flux easily dissolved in the glass allows the grog to float out into the pot.

Low Coefficients The coefficient of expansion of the batch should be studied so that with a more dense, uniform structure, the risk of cracking, due to temperature changes in heating or in use, would be reduced. The coefficient of expansion of the flux would also be important.

The pot of the future, I believe, is one manufactured under as carefully controlled conditions as the spark plug or pyrometer tube. The raw materials are white firing and carefully selected. The structure is uniform, rather fine-grained, the refractoriness depends upon the chemical composition and not upon the coarseness of the grind. In use, it presents a wall suited in chemical composition to the temperature of the furnace and to the glass which comes in contact with it. Not only is the silica-alumina ratio correct but the fluxes are carefully selected as well. The density will be under control and will depend upon the fluidity of the glass at the temperature of melting.

Bausch and Lomb Optical Co.
Rochester, N. Y.

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[1] *Jour. Amer. Ceram. Soc.*, **7**, 583 (1924).

Discussion[1]

W. W. OAKLEY:[2] In the opinion of the writer this paper brings out very effectively the progress of development in the proportioning of pot clay mixes to date and makes a rational prediction of its probable course in the future. There are a few points that I want to discuss from the viewpoint of the glass manufacturer rather than the viewpoint of the ceramic engineer interested not only in the development of pot mixes but in the rapidity of this development.

Among the first reasons given by the author for the slowness of development is his statement made that "Very few glass house superintendents go beyond insisting upon good pots in the most general terms." There appears to be an extremely wide range of meaning to this term "good pots," and whenever the term is used it almost seems to be necessary to consider the viewpoint of the man who uses it. The pot manufacturer's definition of a good pot might be one that is easy to dry, one that will stand considerable jarring stress and when used will give a long life. The glass manufacturer making non-corrosive, easily plained glass will likewise agree with the pot manufacturer that these pots are good. The glass manufacturer making a highly corrosive glass or the manufacturer making a glass plaining up with difficulty except at the highest temperature may find these pots short-lived and condemn them, and lastly the glass manufacturer making an intermediate glass product which is later converted into a different article in automatic machines might be troubled with a stone loss, far more important to him than anything else because it might upset the operation of the automatic machines on a later operation. Consequently, particular care should be used in criticizing pots of one kind or another, because such criticism is seldom forgotten by the hearer and is apt to do an injustice to the person responsible for the pots, whether it be an outside manufacturer or a department of the glass works in question.

On page 207 the statement is made that the need of a Gross Almerode clay is more mental than actual. While this, I think, is essentially true, if time and the necessary money is to be expended in developing the proper blending of American clays, I think that most pot manufacturers will agree with me in the statement that the use of German Gross Almerode clay resulted in a far more fool-proof mix. What I mean is that fewer mistakes and bad results would be obtained by using the German clay than would result from the commercial manufacture of pots from blended American clays and this statement applies not only to pot life but to the ability of the pot to resist jarring stress, improper firing and still be accompanied by the production of good glass of various kinds.

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[1] Submitted Feb. 27, 1925.

[2] Corning Glass Works.

The statement is made that it is possible to get practically any working properties desired, and I assume physical characteristics, within the limits of the silica-alumina ratios given in Table I. It has seemed to the writer that this whole problem of clay composition could not be approached from either the viewpoint of physical properties or chemical composition alone as the pot manufacturer generally has to contend with the question of building a pot for use with a glass of some general composition. A pot of one composition would stand up satisfactorily and give good glass with one kind of glass where it might be absolutely worthless with another. I have found it to be impossible when even considering one plant to keep a definite glass in a pot made for it, and, of course, the commercial pot manufacturer can do nothing in this respect.

Regarding the relation between the silica-alumina ratio and the question of corrosion, we have recently had an instance where two ceramic engineers worked on the same problem but at different times and different places. The problem was to secure a satisfactory tank block for use with a highly corrosive lime glass. The methods and apparatus used were the same and the test furnace in each case was of the same design. In the first case the most satisfactory block composition was found to have a silica-alumina ratio of less than 1.8. The second man on the same problem worked in the other direction and just as definitely proved that the high silica block was more satisfactory, finally arriving at the conclusion that this silica-alumina ratio should be 2.75. It is such conditions as this that tend to perplex the glass manufacturer.

In considering a study of the pot wall after it has reached a point in the furnace where it is not subject to much change, I think it is necessary to consider the type failure before one is justified in thinking about the effect of chemical composition of it. Certainly failures resulting from drying and heating strains or possibly due to poor dimensions and, likewise, a failure due simply to overheating or overrunning due to the furnace man's neglect are not worthy of analysis by chemical methods. To draw conclusions from the chemical analysis of the shell it is necessary to first modify the conclusions by eliminating failures which are due to anything but corrosion. Likewise, in considering corrosion failures it is necessary to consider temperatures, the rate at which glass was being melted and even the possibility of badly mixed pot materials.

In speaking of the pot being equally resistant all over to penetration, there is some question in my mind as to whether this will result in uniform corrosion. In a plant I know of the pot bottoms are practically perfect, but the side walls are not good due to vertical cuts which may be due to filling methods or stress at some time between the making and the filling period. Yet, I have seen these same pots with certain glasses fail uniformly at seven days by bottom penetration with absolutely no trouble on the side walls. With other glasses no corrosion of the bottom at all occurred. Consequently, we again have the importance of the kind of glass being considered in considering resistance to penetration.

When the pot manufacturer is able to maintain a technical control which will result in a uniform run of pots which will fail owing to glass corrosion, I think close consideration of the chemistry of the mixture will furnish wonderful results. However, until we are able to mix clay and deliver it to the pot maker so that it is of uniform chemical composition with grog of uniform sizing and when our pot making methods are so refined that failures due to voids and improper knitting and drying are gone we can do more to improve our pots and clays along these lines than by considering chemical composition as of paramount importance. Also, I am inclined to think that the last sentence presents a large problem for the commercial plant.

Corning Glass Works
Corning, N. Y.

THE USE OF MUFFLE TUNNEL KILNS FOR THE "ARCHING" OF PLATE GLASS POTS[1]

By P. d'H. Dressler and L. T. Strommer

ABSTRACT

Muffle tunnel kilns have now been in use for five years for the purpose of preheating or "arching" plate glass pots. The use of this type of equipment has brought about substantial savings in labor and fuel, and has increased the average life of the pots by approximately 21%.

Introduction

Pots are Expensive One of the heavy items of expense in the manufacture of plate glass is that of the pots in which the glass is melted. The size of these clay containers is very great, varying from circular pots 4 feet 6 inches in diameter and 34 inches high, weighing over one ton, up to oval pots of the same width and height, 6 feet long, weighing 3850 pounds. These pots have thicknesses in some cases up to 10 inches. They are built up by laborious methods from expensive, prepared, washed clays by skilled workmen. It takes many days to build up a pot and, in most factories, months to dry satisfactorily. The investment in a sound dry pot ready for use including the material and labor which enter into its manufacture and the cost of the expensive floor space occupied for such a long period usually amounts to from $50 to $75.

Pots Vary in Quality It is the experience of every plate glass factory that the life of these pots is extremely variable. Not only do the pots from different batches of raw materials made at different times show marked variations but also great differences are found between the behavior of pots made from the same batch at the same time and used, apparently, under identical conditions. Some pots have to be withdrawn from use after only a very few melts due to the development of cracks and leaks. Others will reach forty or even more melts before they become so worn around the ring that the crane can no longer hold them, without having developed any leaks at all. Some pots from the very first melt persistently cast up "stones," others give perfectly clear glass throughout their whole life.

Factors Which Affect Life of Pot There are, of course, innumerable factors which will affect the life and service of a pot. The quality of the raw materials, the nature of the batch, the skill of the maker, the drying process, the preheating to the furnace temperature or the "arching," the skill of the melting furnace tender in controlling the heats and avoiding "burning" of the pots, the care of the crane man in avoiding breakage due to knocking or squeezing the pots, are all factors which must be reckoned with.

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[1] Recd. Dec., 1924. This paper was presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, Feb., 1925. (Glass and Refractories Divisions.)

The Old Way of Arching Pots

The kiln or "arch" used in most plate glass factories for preheating the pots up to the temperature necessary to prepare them for the melting furnace is of the crudest type. In most cases it consists simply of a rectangular box of fire brick in which five pots are set and provided with only one fire hole. The temperature is usually raised to 1800° in about five days when the pots are removed as required and set in the furnace. The control of these arches is crude and due to irregularities of treatment not infrequently pots are cracked in them during their initial heating and cannot be used at all. It is, therefore, apparent that in substituting arching equipment which would give complete control from start to finish and eliminate the possibility of sudden or irregular heating at all stages of the firing, one of the important unknowns among all the factors bearing upon the life of the pots would be removed and this would simplify the study of the requirements to decrease pot costs per square foot of plate glass manufactured.

Car Tunnel Kiln for "Arching"

Some five years ago the Pittsburgh Plate Glass Company, after a careful study of all possible types of equipment, decided to install a muffle tunnel kiln which type they felt would most completely give them the absolute evenness and control they desired. This tunnel kiln has been in operation since August, 1919. Since that time three others have been installed and put into operation, the most recent one at the plant of the Ford Motor Company, Glassmere, Pa. These installations have uniformly given the very best of service. Up to this time nothing has appeared in the literature of the glass or refractories industries regarding them and it appears to the authors that some of the details of the operation and of the results obtained would be interesting at this Colloquium of the Glass and Refractories Divisions.

The Car Tunnel Kiln

The design of a tunnel kiln for arching glass pots involved a number of problems not met with in any other ceramic industry. The essence of most tunnel kilns is that they shall operate continuously with cars placed and taken out at regular intervals. In the glass plant the pots are needed only for 18 hours out of the 24, during which the casting is being carried on, and only as required to replace the pots removed from service. Sometimes three or more pots will be required in quick succession. At other times there will be no call for any pots at all for 48 hours. Furthermore from the very nature of the operation such a kiln has no cooling zone and provisions have to be made to withdraw the pots at the highest temperature.

Manifestly, if regularity and evenness in preheating are desired, it will be fatal to push in four fresh cars at the entrance end, in an interval of fifteen minutes, if that number of cars is suddenly required from the exit end, since this would involve a sudden jump in temperature of the pots in the danger periods of the heating cycle. The tunnel kiln, therefore, must have a reserve of hot pots in the furnace zone which can be withdrawn without moving forward the whole train at more than the regular operating speed.

If the pots are withdrawn from the hottest section of the kiln for a space of, for instance, 20 feet back from the door, it is apparent that the floor and the tracks, being no longer covered by the car bottoms, are exposed to the full radiation of the crown. This introduces the double danger of destroying the floor by overheating it and subsequently, when the cars are gradually pushed up over the hot floor, of overheating these also by means of the stored heat in the latter. Then there is the difficulty of providing a reasonably tight door at the exit end which will permit of pots being withdrawn at about 2000°, the temperature required in most installations.

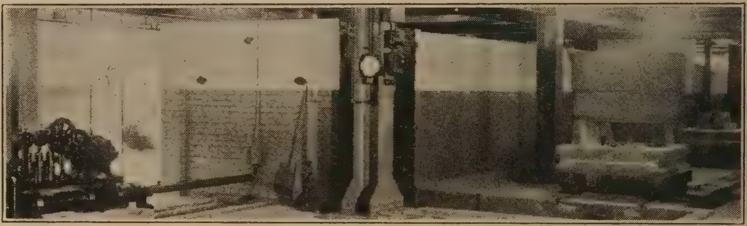

Fig. 1.—Entrance end of pot arching tunnel kiln showing method of loading pots on the cars and the hydraulic propeller.

The "Dummy" Car at Exit End

Figure 2 shows the exit end of a tunnel kiln in which these difficulties have been successfully encountered. The door is composed of a steel frame lined with insulating brick, operated by means of an air cylinder. Between the door and the hottest portion of the kiln is what is known as a "dummy car" or a short car bearing a brick structure closely conforming to the side walls and arch of the kiln, which serves the double purpose of preventing the full heat of the kiln from reaching the door and acting as a reservoir of heat to prevent the last pot in the kiln from being cooled by proximity to the door. This "dummy car" is connected to a long rack by means of which it can be withdrawn from the kiln across the transfer car and into a small fire brick house. By means of an automatic device, when the "dummy car" is pushed by means of the rack into contact with one of the kiln cars, it couples itself to the latter and the two cars are then moved as one by means of the rack. The operation of the kiln, then, is as follows:

Let us suppose that the full length of the kiln is occupied by a train of cars loaded with pots and that the "dummy car" is directly inside the exit door. When a pot is required, the exit door is opened and, by means of the rack, the pot-bearing car and the "dummy" are simultaneously withdrawn. The transfer car is in place and the dummy car passes over it. As it does so the coupling device is automatically tripped leaving the pot-bearing car on the transfer while the "dummy car" passes into its house. The exit door of the kiln is then closed and the transfer car moved out beneath the furnace hall crane which picks off the hot pot and transfers it to one of the furnaces. The kiln car is then moved onto the return track where it is allowed to cool before a fresh dry pot is set upon it, while the transfer car is moved back to the position directly in front of the exit door of the kiln. The latter is raised and, by means of the rack, the "dummy car" is returned into the kiln. If necessary it can be pushed in far enough to pull a second or a third car immediately. When the kiln propeller is

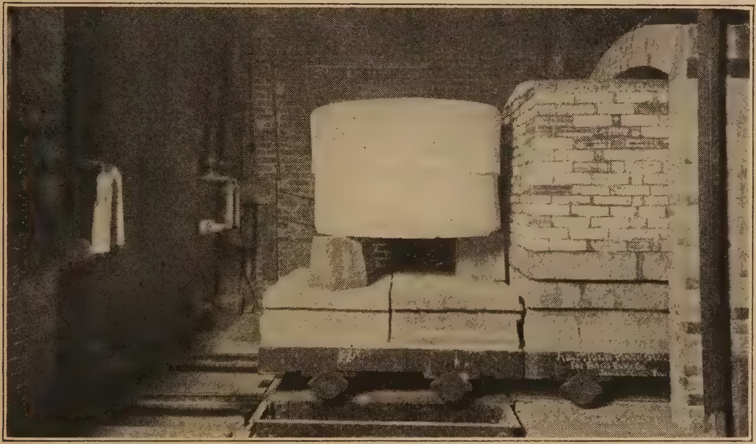

FIG. 2.—Exit end of pot arching kiln. On the left hand side is seen the steel door of the tunnel kiln. On either side of the door are the natural gas burners projecting their flames down the tunnel kiln combustion chambers. To the right is the brick structure used to house the "dummy car" during the time it is withdrawn from the tunnel kiln. The "dummy car" is shown coupled to a kiln car bearing a pot just before the coupling device is automatically tripped, leaving the car, bearing the pot, on the transfer. The next operation is to move the transfer under the casting ball crane and remove the pot.

started up on taking out the first pot, a fourth pot can be reached within a few minutes.

Protection of Kiln Floor It will be seen that when this process is completed a considerable length of kiln floor is exposed to the full heat. In order to prevent damage it is composed of a steel plate, air cooled on the under side and covered with a thin layer of insulating material on the upper side. The latter prevents direct heating of the metal and at the same time has so low a heat capacity that after it has become heated by exposure to the full radiation from the arch, no trouble on the under sides of incoming cars is caused by it.[1]

Length of Kiln The lengths of the tunnel kilns vary according to the desired production and the size of the pots. The shortest of the kilns is 151 feet and the longest 170 feet. The least number of pots in a kiln is 26 and the greatest 33. The time of arching in most installations is from 84 to 96 hours. In one of them, however, it has been found possible to run on a 54-hour schedule. In this case the batch is of a sandy open nature and will stand more rapid heating. The temperature at the delivery end varies from 1850 to 2000° on different installations.

In two of the plants where tunnel kilns have been built these supply the full requirement of arched pots. In the other two the kilns were designed to have a capacity of less than the maximum requirement and in these plants part of the pots are being supplied, during the peak load periods, from the old type of pot arching furnaces.

The Economies of Car Tunnel Kiln for Arching

After five years of operation it is possible to state that the tunnel kilns have shown, in comparison with the old arches, three distinct sources of economy, *viz.:* labor, fuel and increased life of pots.

Labor In all of the installations the hot pots are delivered beneath the casting hall crane runway. The pot is picked off the car by means of the same carrier that is used to transfer the pots to and from the furnaces and the casting table. The special wheeled carriage and the large number of men needed to reach and handle the pots in the arches are no longer required. One man is able to take care of all the operation of the tunnel and on natural gas no attention at all is required during the intervals in which casting is not taking place.

Fuel The average amount of fuel per pot required in the intermittent arches has been given to the authors as 22,000 cubic feet of natural gas. The fuel consumption in the different tunnels varies according to the rate of operation, the lowest average fuel consumption being 4600 cubic feet and the highest 8000 cubic feet per pot. The fuel saving is, therefore, from 63% to 79% and at 35 cents per M cubic feet for natural gas this amounts to from $4.90 to $6.10 per pot.

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[1] The construction and method of operation of the exit end of the pot arching tunnel kilns are protected by patents.

Pot Life

Pots cease to be of any use when, owing to the development of cracks or leaks, they will no longer hold glass, or when they start to throw up so many stones that the glass melted in them is not satisfactory. As already stated there are very many factors in addition to the "arching" which have an influence upon the service of the pots, and it is apparent that any improvement in the method of "arching" will show its effect much more in the early life of the pots than in the later, since by the time a pot has been used 20 to 40 times so many influences have had an effect upon it.

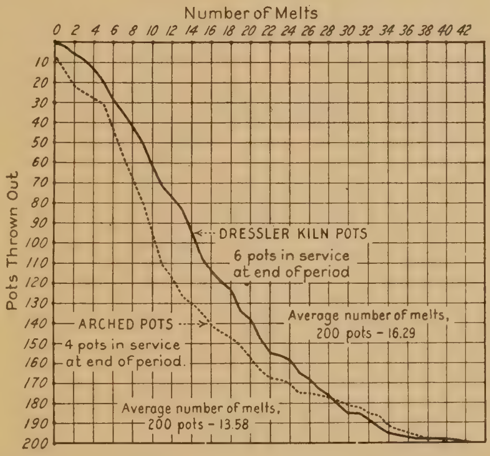

FIG. 3.—Cumulative curve showing life of pots arched in intermittent arches and in tunnel kiln.

Furthermore, to make any comparison between the results of the different methods of "arching" upon the life of the pots it is useless to compare the life of pots "arched" in tunnel kilns with the life of pots "arched" in the old fashioned manner in the previous month or the previous year. The only satisfactory way is to compare the life of the same batch of pots passing through the arches and the tunnel kiln simultaneously and being used in the same melting furnaces at the same time. In the case of the two plants in which the production of pots is divided between the tunnel kilns and the arches, it has been possible to make this comparison. Very careful and complete records were made which are set forth in the tables.

In case of plant No. 1 a very careful check was made upon the life of the first 200 pots taken from the tunnel kiln and of 200 pots simultaneously arched through the old intermittent arches. The pots were put into service during a period of six weeks and their life was followed through for the following six weeks. At the time that the observations were concluded all of the pots had been discarded except six from the tunnel kiln and four from the arches. The full data are shown in the following table and are summarized in the accompanying curves (see Fig. 3):

Comparative Life of Pots in Kilns and in Arches

Life of pots in melts	Number of pots scrapped		Cumulative number scrapped		Total melts		In service at end of period	
	Kiln	Arches	Kiln	Arches	Kiln	Arches	Kiln	Arches
0	1	7	1	7	0	0		
1	1	7	2	14	1	7		
2	4	8	6	22	8	16		
3	3	3	9	25	9	9		
4	5	3	14	28	20	12		
5	6	3	20	31	30	15		
6	9	13	29	44	54	78		
7	6	13	35	57	42	91		
8	8	11	43	68	64	88		
9	7	12	50	80	63	108		
10	12	16	62	96	120	160		
11	10	15	72	111	110	165		
12	5	6	77	117	60	72		
13	6	9	83	126	78	117		
14	12	4	95	130	168	56		
15	12	4	107	134	180	60		
16	7	7	114	141	112	112		
17	5	3	119	144	85	51		
18	4	3	123	147	72	54		
19	11	4	134	151	209	76		
20	4	6	138	157	80	120		
21	10	6	148	163	210	126		
22	7	4	155	167	154	88		
23	1	1	156	168	23	23		
24	2	2	158	170	48	48		
25	7	5	165	175	175	125		
26	3	0	168	175	78	0		
27	5	1	173	176	135	27		
28	3	1	176	177	84	28		
29	5	2	181	179	145	58	1	
30	4	2	185	181	120	60	3	1
31	0	1	185	182	0	31		
32	3	3	188	185	96	96		
33	4	1	192	186	132	33	1	1
34	3	5	195	191	102	170	1	1
35	1	2	196	193	35	70		
36	1	2	197	195	36	72		
37	1	1	198	196	37	37		
38	0	2	198	198	0	76		
39	0	0	198	198	0	0		
40	0	2	198	200	0	80		1
41	1		199		41			
42	1		200		42			
Totals	200	200			3258	2715	6[1]	4[1]
Av. melts					16.29	13.58		

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[1] Those pots still in service at the end of this period of observation were considered as having been thrown out at that time and melt.

The curves are plotted in such a way as to show the cumulative number of pots thrown out at successive melts. The area between the two curves represents the total difference of life obtained by the different methods of arching. It will be noted that there were very markedly less pots thrown out in the early melts of the tunnel kiln pots than of the arched pots. Seven arched pots were found cracked when removed from the arches and gave no service at all. One tunnel kiln pot is shown as having given no service. This pot was one of the first withdrawn from the tunnel kiln. It emerged sound but was broken by the crane-man who was not yet familiar with the lifting of the pots off the tunnel kiln cars.

The greatest divergence between the curves occurs around 12 melts. From the tunnel kiln pots 77 were thrown out with 12 or less melts as against 117 from the arched pots. From this point forward the tunnel kiln pots naturally show a higher rate of loss than the arched pots since there are more of them left and the various influences of age and service are beginning to tell. After 18 melts the curves approach each other rapidly. By this time all influence of the arching has been eliminated and at the higher melts the curves are practically identical.

The total number of melts from the tunnel kiln pots was 3258 with an average of 16.29 per pot and from the arched pots 2716 with an average of 13.58 per pot. If the tunnel kiln pots had shown the same average life as the arched pots exactly 40 more would have been required to give the same number of melts. Assuming a cost of $60.00 per pot this means that in the first six weeks' operation of the kiln the increase of pot life showed a saving of 40 × $60, or $2400.00.

In case of plant No. 2 a record was taken of all the pots removed from the tunnel kiln and the arches for the first five months of the former's operation, and subsequently the history of all these pots was followed through until every one of them had been thrown out of use. The results are shown in the following table:

COMPARATIVE LIFE OF POTS IN KILN AND ARCHES

	Pots arched		Total melts		Average per pot	
	Kiln	Arches	Kiln	Arches	Kiln	Arches
1st month	117	106	1785	1196	15.26	11.28
2nd month	93	94	1317	1327	14.16	14.12
3rd month	123	59	2197	993	17.85	16.83
4th month	132	50	2264	740	17.15	14.80
5th month	111	56	1952	718	17.59	12.82
Totals	576	365	9515	4974		
Average melts per pot for whole period					16.52	13.63

The difference in life here is fractionally higher than in the case of plant No. 1. Unfortunately, sufficiently detailed data are not available to draw up the same kind of a curve. However, if the tunnel kiln pots had shown the same life as the arched pots, to make 9515 melts, 697 pots would have been required. The difference between this figure and 576, or 121 pots, is the number saved by the use of the tunnel kiln for arching. At $60.00 per pot this amounts to $7260.00. It will be noted that when this kiln was started up the pot requirements were divided more or less evenly between the tunnel and the intermittent arches but gradually, as the results obtained were checked, the proportion of pots from the tunnel kiln was increased. At the present time the tunnel kiln is supplying from 75 to 85% of all the pots used in a seven-furnace plant.

The figures above, quoted from the operation of these two plants, are taken over a sufficient period of time to justify the claim that the use of the muffle tunnel kiln with its exact control and freedom from sudden changes can and does bring about a substantial improvement in the services obtained from the pots amounting in the cases quoted to an average increase of life of approximately 21%.

CLEVELAND, OHIO

Discussion

C. E. FULTON:[1] This paper covering the use of the muffle tunnel kiln for the arching of plate glass pots is very interesting and the results which we have obtained with one of these kilns in general check with the conclusions that have been drawn.

However, there is one improvement in the modern plate glass factory which throws a different light upon the economy claimed for the tunnel kiln in labor saving. Instead of having a gang of men to take a hot pot from the arch, it is now the practice to have an electrically operated truck fitted with tongs with which one man can go into a pot arch and remove a hot pot which is to be set into the furnace. This man is one of the regular casting hall organization and the work of removing a pot from the pot arch is only one of his many duties. The fact that the hot pot coming from the tunnel kiln is handled by the regular crane man does not eliminate the man above referred to from the casting hall organization, and while the amount of labor is somewhat less, there is no saving for the company except the cost of operating the electric truck.

It is stated that the fuel consumption per pot is from 4600 to 8000 cubic feet of natural gas when arched in the muffle tunnel kiln. In the manufacture of plate glass on a large scale, it is essential that there be no interruptions in the casting hall work which would interfere with production. It is therefore necessary whenever a defective pot is thrown out of the furnace, to have another new pot hot and ready to set. For this reason we have found it necessary to build three storage arches, which are kept hot and filled with pots from the tunnel kiln. If the fuel for these auxiliary or storage arches, which we deem necessary, is included with that consumed by the tunnel kiln, the average gas consumption per pot is approximately 18,000 cu. ft. The fuel per pot consumed in the regular pot arches shows a great variation according to whether the pots are used as soon as they are heated up to the required temperature, or whether they are permitted to remain in the arch for several days after they have been brought up to temperature. The figure of 22,000 cu. ft. per pot given by Mr. Dressler was an average figure at our plant when we were using a smaller pot than we are at present. Using a large pot weighing approximately 3800 pounds, the gas per pot when arched in the regular pot arches is around 35,000 cu. ft., although one month last year 103 pots were put through the regular arches with an average gas consumption of 18,500 cu. ft. per pot.

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[1] Recd. March 8, 1925.

Since the installation of the tunnel kiln we have arched 16,297 pots of which 71% were arched in the tunnel kiln and 29% in the regular pot arches. During this time we have had approximately 1% of the pots from the tunnel kiln broken during the arching period, while in the regular pot arches 3% of the pots have been broken. The greater part of the breakage in the tunnel kiln has undoubtedly been due to pots being set which contained some invisible defect caused either in the making or drying. The same thing applies to pots in the pot arches, and in addition some of the breakage in the arches has been due to pots made from experimental batches. No experimental pots are put through the tunnel kilns because when breakage does occur in the tunnel kiln, it is liable to cause serious damage. On two occasions over a period of more than five years a pot breaking in the tunnel kiln has caused damage which necessitated shutting the kiln down for repairs. In the first case the kiln was out of operation for 12 days and in the second case for only 6 days.

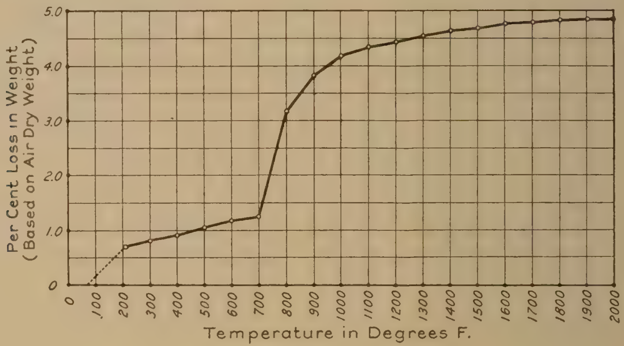
We find in general that the life obtained from pots arched in the tunnel kiln averages about 2 melts better than those arched in the regular arches. This checks rather closely with Mr. Dressler's statement of an increase of 20% in life.

Mr. Dressler states that the ordinary pot arches found in plate glass factories are very crude. This statement is correct, but it might be pointed out that even with this crudeness, very good results have been obtained over a long period of years. This is no doubt due to the fact that the preliminary heating or arching of a plate glass pot is really a very simple operation and if performed with a reasonable degree of intelligence, good results will be obtained.

The ordinary plate glass pot batch contains anywhere from 40–60% of non-plastic material ground to pass an 8- or 10-mesh screen. The amount of volatile matter which is driven off during the arching period seldom exceeds 5% (mostly moisture and water of hydration), and the firing shrinkage taking place during this period approximates .5%. In Fig. 1 is shown the percentage of loss in weight of a typical pot batch when held at various temperatures until it reached constant weight. This curve shows that 14% of the total loss occurs by the time the pot has been heated to 210°F and that 86% of the total loss has been driven off when a temperature of 1000°F has been reached. Therefore, if reasonable care is exercised up to a temperature of 1100 or 1200°F, no trouble should be experienced.

For the best results in arching, the pot itself should be thoroughly dried when set in the arch, and the arch and stack connected with it should be dry so that there will be sufficient draft to carry off the moisture as it is evaporated. We have found it advisable to store pots in a hot room at a temperature of 135–140°F for approximately 5 days so that when they are set in the arch or tunnel kiln, the free moisture will not exceed .75%. Each individual pot arch is equipped with a recording pyrometer and the rate of heating to be followed marked plainly upon the chart for the guidance of the pot arch fireman. When these precautions are followed, good results are obtained from the ordinary type of pot arch.

Pot arches are not insulated in order to reduce the fuel consumption because the time required for cooling would be increased and thus a larger number of arches would be required.



It used to take months to dry a pot satisfactorily. Pots which formerly took 6–8 months to dry are now being dried successfully on a commercial scale in 8 days by the use of a humidity drier.

In planning a new factory the tunnel kiln method of arching would certainly be used. Where a factory is already equipped with sufficient pot arches the amount of saving in a tunnel kiln is greatly decreased. The production at the Ford City plant has increased to such an extent that we are now considering the installation of a second tunnel kiln.

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THE EFFECT OF RED HEARTS IN FIRE CLAY BRICK[1]

By M. C. Booze[2]

ABSTRACT

Laboratory tests made on two brands of fire clay brick indicate that red hearts, which are normally considered as being detrimental, add to both the hot and cold strength and would not be objectionable except in furnaces operated at a low temperature, and in which spalling is an important item. Results of load, reheating and spalling tests are given, together with porosity and iron oxide determinations. A short discussion of the causes of red hearts is also included.

Introduction

Red hearts, or cores, occur in a rather large percentage of the fire clay brick manufactured and have always been considered objectionable, both by the manufacturers and consumers. Data which have been obtained in this laboratory make it apparent that these objections are unwarranted and the results which are given below are presented in the hope that they will help to clarify the matter.

The chemical and physical phenomena producing this discoloration have been discussed by Orton.[3] Here the conclusion is reached that the color in the center of a brick is made stronger or brighter by the iron present in the clay first being reduced and later reoxidized, while that in the outer portions remains in the oxidized condition from the first. This conclusion is evidently justified, it being well known that more intense colors are produced in firing iron bearing clays by alternate periods of oxidation and reduction than by continuously oxidizing or reducing firings. The reduction at the center, which causes the core, results from carbonaceous matter which is present and which is more difficult to burn out in the interior than at the surface. The condition is aggravated if the brick are wet, since, in this case, the oxidation of the carbonaceous matter is retarded, and by the time the brick have been dried by the kiln gases the latter have approached the temperature at which the iron is reduced by the combustible material in the clay.

The fact that some clays are subject to this discoloration while others are not is explained by differences in iron content, amount and kind of carbonaceous matter present, and relative density of the products.

In the reduced condition the iron is active as a flux and from the results obtained during this investigation it appears that a portion of the iron in the cored brick had been reactive in this way, although it had been suffi-

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[1] Presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, February, 1925. (Refractories Division.) Received Jan. 2, 1925.

[2] Senior Fellow, Refractories Manufacturers Association Fellowship, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

[3] "Rôle Played by Iron in the Burning of Clays," *Trans. Amer. Ceram. Soc.*, **5**, 377 (1903).

ciently changed by reoxidation as not to have an appreciable effect upon the refractoriness of the product as tested. These conclusions are based upon the fact that the hot and cold strengths of the cored brick are both noticeably higher than those of the uncored ones.

The Investigation

The brick used for the tests here described were obtained from two different manufacturers. Those in each lot were made from identical mixtures of clays as nearly as was practicable and received the same heat treatment, being fired together. For the purposes of our tests, therefore, the only difference between the brick in one lot was that some of them had typical "red hearts" and others were of the usual color throughout.

The following results were obtained from tests on these samples:

BRAND A

	Samples with red cores	Uncored samples
Load test, 25 lbs. per sq. in., 1350°C, for $1^{1}/_{2}$ hrs.	First lot 5.56% deformation Second lot 5.68% deformation	First lot 9.23% deformation Second lot 8.00% deformation
Reheating at 1400°C for 5 hours	0.50% expansion	0.85% expansion
Spalling as received	Failed after $5^{1}/_{3}$ dips (average of 3)	Failed after 15 dips (average of 3)
Spalling after reheating	Failed after $2^{1}/_{3}$ dips (average of 3)	Failed after 2 dips (average of 3)
Modulus of rupture—cold	1040 pounds per sq. in.	690 pounds per sq. in.
Porosity	18.4%	20.5%
Fe_2O_3 content	2.89%	2.99%

BRAND B

	Samples with red cores	Uncored samples
Load test, 25 lbs. per sq. in., 1350°C for $1^{1}/_{2}$ hours	First lot 3.98% deformation Second lot 1.01% deformation	6.12% deformation 4.79% deformation
Reheating at 1400°C for 5 hours	2.03% expansion	1.12% expansion
Spalling after reheating	Failed after 3 dips (average of 4)	Failed after $3^{1}/_{2}$ dips (average of 4)
Modulus of rupture	751 pounds per sq. in. (average of 10)	419 pounds per sq. in. (average of 10)
Porosity as received	27.8%	28.0%

Discussion of Results

Load Tests In each load test two bricks were tested in one furnace at the same time, one being a cored and one an uncored specimen. In this way any inequalities as to temperature, atmosphere, etc., were removed.

A considerable difference is noticeable between the cored and the uncored brick in these tests, the former deforming less in each case. As previously explained, this is probably due to the strong bond developed by the iron during the period that it was in the reduced state. A similar effect may be obtained by hard firing, although in this event more of the fluxes take part than just the iron oxide.

Reheating Tests All of the brick tested expanded in this test, the expansion being greater on the uncored samples of one lot than those having red hearts, and the reverse being true on those of the second lot.

Except in those cases where the expansion is due to the formation of a vesicular structure, or where it is abnormally high, it has not been found possible to draw any definite conclusions from the results of the reheating test, especially with regard to the behavior in actual service.

The rate of heating appears to be more of a determining factor in many cases than either the composition or the temperature and a slow schedule such as is encountered in the majority of industrial furnaces during the initial heating up of the lining has but little effect in producing permanent expansion.

The reheating test is of considerable value, however, in preparing the brick for the spalling test, and it was largely for this reason that the samples reported on here were refired.

Spalling Tests The results of this test show no appreciable difference between the cored and uncored samples when they have been reheated before spalling. When tested without reheating, the uncored samples of one lot gave appreciably better results than those containing red hearts.

The standard method of test calls for reheating before spalling and from the very large number of tests made in this laboratory it is evident such is the logical procedure. Brick which are made from comparatively poor clays and given a soft firing may show very good results in the spalling test if tested as received, due to the fact that they are not maintained at a high temperature for a sufficiently long time in the test to produce the vitrification which would normally take place in service. This point is illustrated by the results obtained on the "A" brand of brick. In this case reheating the uncored samples had a very great effect upon the spalling test results and evidently produced a much more brittle body than did the red hearts alone.

Cold Strength and Porosity The modulus of rupture is considerably higher on the cored samples of both lots than on the uncored ones. In one case this increase in strength was apparently gained by merely sintering the grains together at the points of contact, as there was no appreciable difference in porosity between the cored and uncored bodies. In the second case a consolidation of the mass accompanied the increase in strength, the porosity being reduced from 20.5 to 18.4%. This reduction in porosity, however, is small. Differences of this order occur in brick which are, for all practical purposes, made alike.

Iron Content These determinations, which show a difference in iron content between the cored and uncored parts of an amount less than that which may occur from variations in the clays and errors in the analyses, were made to prove that there was no concentration of iron in the highly discolored portion.

Conclusions

The results of these tests show that instead of being inferior, fire clay brick containing red hearts are, for many purposes, superior to those of equivalent composition, grind, etc., but which do not have the red hearts. The former are stronger, would deform less in service and in all probability would show less shrinkage than those of the usual color. The core affects the brick in much the same way as hard firing, the beneficial results of which are evidenced by the growing demand from consumers for hard-fired products. For low temperature furnaces, where spalling is the major item producing failure, the red hearts would be objectionable.

The cored brick are unsightly in appearance and this has doubtless been the cause for many complaints. The color difference is so marked as to make it appear that there is a concentration of iron in the cored zone, which, as has been shown, is not the case.

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PITTSBURGH, PA.

Discussion

G. A. BOLE:[1] Mr. Booze's problem is most interesting to me from the standpoint of fundamental data. Red cores both in fire brick and face brick have been considered a defect, a sort of an indictment of poor firing practice and indeed they do go hand in hand. This phenomenon is quite common in the face brick industry where fire clays containing iron and sulphur are used, with or without much carbon. Mr. Booze, quoting Dr. Orton, suggests that carbon reduction with subsequent oxidation is probably the cause of the red core. I would like to ask Mr. Booze if he has the chemical analysis of the original clay and of the cored and uncored ware.

I am under the impression that the sulphur gases rather than the carbonaceous matter are the principal reducing media in most cases at least, although the actions will overlap in some cases. The carbon will of course retard the oxidation of the sulphur when there is much organic matter present thus aggravating the situation. The idea that sulphur rather than carbon is the culprit comes from the fact that draw trials from a commercial kiln may be perfectly free of black core (having been burned out) and still later a red core will develop. The ware may "remain open" for days thus giving the iron abundant time to reoxidize if no other factor were retarding the oxidation. The sulphur oxidation or "blue smoke" period seems to be where the red core is "burned out," the assumption being that if this period is run through too quickly the reducing sulphur gas, arising from the decomposition of iron sulphur compounds, will not be burned out of the clay soon enough to give the iron a chance to reoxidize before the body "closes up." The sulphur may probably be in the fuel in some cases, being absorbed by the clay, but in most cases at least it is in the clay.

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[1] Superintendent, U. S. Bur. Mines, Ceramic Expt. Station, Columbus, Ohio.

As pointed out by Mr. Booze, a wet bottom holds back the temperature in the bottom of the kiln, thus subjecting the ware to a sudden rise in temperature when it is finally dried out. This explanation holds whether the reduction is due to carbon or sulphur. We have found, however, that large quantities of sulphur gases from the coal are absorbed by the ware in the bottom of a wet kiln and fixed there by chemical combination—very largely with the iron. To just what an extent this is a factor in later developing a red core we do not know. The red core under the microscope appears to be due to a film of a reddish brown iron stain on the clay grains.

In extreme cases of red coring specks of a brilliant red glass will show up when examined under the microscope. These specks, so far as observed, are always in the slag craters caused by the fusion of the ferrous silicate. I have thought of them as iron in colloidal suspension in a glass although we have not made a study of the phenomenon. In cases where the red core is less pronounced this red glass does not generally show up, all the color being due apparently to the stain on the clay grains.

M. C. Booze:[1] Unfortunately, no sulphur determinations were made upon any of the materials or products covered in this paper. As Mr. Bole has pointed out, sulphur from the decomposition of sulphides would produce a reducing action upon other iron compounds in the same way as carbonaceous material. The coring could then be caused by either or a combination of both, according to the amounts which were present. There are some fire clays used which contain a relatively large amount of pyrite, and which, to the writer's best knowledge, do not produce red cored brick. This lack of coring may, of course, be due to a well regulated firing process, or to the fact that the iron is present in particles of comparatively large size.

Whether the reduction is due to carbon or sulphur, the net result should be the same and the data given here showing the effect of the core should hold for either case.

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[1] Reply to Mr. Bole's Discussion, by Mr. Booze. Received March 16, 1925.

AN ANALYSIS OF THE SUSPENSION OF ENAMEL BY CLAY IN TERMS OF THE COLLOID THEORY[1]

By Emerson P. Poste[2]

ABSTRACT

A detailed review of the literature on the action of electrolytes and organic matter on clays is given.

The problem of the "setting up" of enamel has held the attention of many investigators. But numerous as the efforts seem to have been the published practical results are very meager. This statement is made with no malice, for the writer has done his share of "floundering" along this line and undertakes the present effort very humbly. What we have been groping for is an idea as to the fundamental principle of the suspending of enamel by clay, with due regard to the action of "vehicles" added in "setting up," and a means of using such findings in the shop.

As we look back we feel that our main weakness may have been in the lack of a definite idea of the mechanism of the process and in the use of a wrong conception of the physical properties of the enamel slip as related to its application to the ware.

Possibly a rather definite hypothesis as to the functioning of clays in processing enamel would be of value. The colloid theory has been profitably applied to clay under other conditions of use, why not to enamels?

An effort has been made by the writer to formulate a definite statement of the colloid theory as applied to the processing of enamel by the wet method. This is based largely on the ideas of others as quoted from the literature. Quite naturally there are differences of opinion on many of the details.

General

As a batch of finely ground enamel with clay and water leaves the mill, it is probably a mixture of non-colloidal enamel and clay particles, colloidal enamel and clay particles, and water with such materials in solution as may have dissolved from the enamel or other materials during grinding.[3] The colloidal matter is probably in the sol form. These statements are on the assumption that no "vehicle" has been included in the mill charge.

The addition of the electrolyte used in "setting up" probably flocculates the colloidal matter forming a gel. If the amount of water is not too excessive to allow the gel and the solid matter of the system to form

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb. 1925. (Enamel Division.)

[2] Director of Laboratories, The Pfaudler Company, Elyria Division.

[3] Ashley, "The Colloidal Matter of Clay and Its Measurement," U. S. Geol. Surv., *Bull.* **388,** p. 17; Ashley, "Technical Control of the Colloidal Matter of Clays," Bur. Stand., *Tech. Paper* **23,** p. 33.

something of a continuous structure, the non-colloidal particles are held up by it. If the water is excessive, the structure is not continuous and cannot hold up the larger particles, and settling results.

Proper working qualities under a given set of conditions of application probably depend on a correct adjustment of the elements which enter into the above general mode of action.[1]

Suspending Power of Clay

"The ability of a clay to take up and to hold in suspension relatively large amounts of foreign material (such as sand, powdered minerals, etc.) without destroying its other properties is to be attributed to the presence of colloidal material which surrounds the foreign particles and thus binds them together."[2] There is probably a material difference in clays as to the amount of colloidal matter involved. "Almost any mineral, as well as various soluble salts, may be present in clays and modify the properties somewhat."[3]

Action of Electrolytes on Clay Suspensions

It is generally thought that the dispersed particles of clay are negatively charged.[4] When, through the addition of an electrolyte, charges of opposite sign are available, the negative charges are no longer effective and flocculation results. "The positive ion of the electrolyte is of most influence in effecting the precipitation, the acid ion taking little part."[5] Some hold that precipitation by an electrolyte is a definite chemical reaction, a double decomposition in fact.[6] Electrolytes are classified as "flocculators" and "deflocculators." The former class includes acids and neutral salts and the latter the stronger alkalis and the organic colloids. As to the quantitative phase of the problem, it is generally held that the valency rule applies.

To produce complete precipitation a certain concentration of ion is necessary.[7] This is termed by some the "threshold concentration," by others the "iso-electric" point.[8] Further additions have no increasing effect. If an excess of electrolyte is added all at once, the iso-electric point may be passed before coagulation occurs and the particles acquire a charge opposite to the one they had originally.[1] One investigator of colloid suspension says, "The velocity of coagulation is influenced by the manner of adding the electrolytes. The velocity is less the more dilute the solution by means of which the electrolyte is introduced. If a part of the electrolyte is introduced insufficient to cause coagulation and time allowed to elapse before addition of the remainder, the rate of coagulation is less than when the electrolyte is added all at once. The retardation is greater the greater the amount of the first addition and the longer the time elapsed between additions. By this method it seems to be possible to obtain a sol that will be permanently stable in the presence of a concentration of electrolyte that would coagulate if added all at once."[2] Another writer states that "the manner of adding the reagent has a marked effect on precipitation.....When added very slowly or a little at a time, a much larger amount is necessary for complete precipitation.........The slower the reagent is added the greater is the excess."[3]

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[1] Ashley, Bur. Stand., *Tech. Paper* **23**, p. 16.

[2] *Ibid.*, p. 38.

[3] *Ibid.*, p. 33.

[4] Ashley, U. S. Geol. Surv., *Bull.* **388**, p. 17, 22.

[5] *Ibid.* p. 18, 22; Ashley, Bur. Stand., *Tech. Paper* **23**, p. 16; Alexander, "Colloid Chemistry," p. 33.

[6] Taylor, "Chemistry of Colloids," p. 109.

[7] *Ibid.*, p. 95.

[8] Ashley, Bur. Stand., *Tech. Paper* **23**, p. 16.

The coagulating effect of salts varies with the valence. With certain sols it has a value of 1–60–600 for mono-, di- and trivalent ions.[4] With clays the effects are not so great. As to the relation between the concentration of colloid and electrolyte, it has been found in some cases that the concentration of anion necessary to produce flocculation increases with decreasing concentration of colloid for univalent, is practically constant for divalent, and varies almost directly with the concentration of the colloid for trivalent anions.[5] Certain studies in connection with the use of magnesium sulphate have led the present writer to the conclusion that the above statement as to bivalent anions applies to clay suspensions of enamel. Ashley states, however, that "the concentration of reagent in the solution may be of less importance in determining the final state of the system than the ratio of reagent to clay."[6]

A somewhat different point of view is suggested by one writer who says that "the plasticity of clays depends on the amount of hydroxyl ions present in the water. When this is large, the negatively charged clay particles will go into colloidal suspension. When the hydroxyl concentration is depressed, as by the addition of acid or depression of temperature, the clay will assume the gel condition and become plastic. For decreasing plasticity may be used all bases, organic and inorganic, all salts of strong base with weak acids, which hydrolytically split off OH ions in large amounts. To this classification belong potash, soda, salts of phosphoric acid, salts of silicic acid. Neutral salts with very few exceptions appear to behave indifferently. As indifferent salts are sodium chloride, sodium sulphate, potassium nitrate, magnesium chloride, and others. The causes of the abnormal behavior of some are not yet exactly known."[1] This general view is refuted by Ashley who says, "It seems more logical, though perhaps more difficult in details, to refer plasticity to the gel structure of the clays themselves, than to the vehicle. It must be allowed that the condition of the water will have effects of the nature assigned above. But as clay is plastic when wetted with materials not containing hydroxyl ions, hydroxyl can by no means play the principal part."[1]

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[1] Alexander, *op. cit.*, p. 32.

[2] "A Protection Effect in Suspensions Obtained by the Addition of Electrolytes in Amounts Too Slight to Involve Coagulation," *Chem. Abs.*, **18,** 3511(1924).

[3] Taylor, *op. cit.*, p. 98.

[4] Ashley, U. S. Geol. Surv., *Bull.* **388,** p. 22; Alexander, *op. cit.*, p. 33; Taylor, *op. cit.*, pp. 106, 109; Ashley, U. S. Bur. Stand., *Tech. Paper* **23,** p. 16.

[5] Barton and Bishop, "Coagulation of Colloidal Solution by Electrolytes—Influence of Concentration of Sol," *Jour. Phys. Chemistry,* **24,** 712 (1920).

[6] Ashley, Bur. Stand., *Tech Paper* **23,** p. 45.

The recent application of the conception of hydrogen ion concentration has been a most fruitful effort in a great variety of industries. The work of F. P. Hall[2] suggests a possible relation between hydrogen ion concentration and the flocculation of clays. It is not too much to hope that work along this line would bring results in connection with the present problem.

Effect of Organic Matter in Clay

The relation of the organic matter in clay to its colloidal properties is considered an important point by many. Recent discussions on the floor of this SOCIETY have dealt with this subject. Possibly some organic materials act as protective colloids.

"When a very stable sol in the presence of a less stable sol of the same sign is acted upon by an electrolyte that will not precipitate the former, but would precipitate the latter if alone, the influence of the more stable sol is often sufficient to 'protect' the less stable sol from coagulation. Non-colloidal substances can exercise protection. Gelatine is a common 'protection colloid' for many substances of small-sized ions. The colloids of clay may carry into suspension solid particles that are wholly non-colloidal by ordinary ideas."[3]

"Mixtures of two colloids of opposite signs cause a precipitation which is complete at a definite proportion; but addition of an electrolyte capable of precipitating one of the two colloids prevents their mutual precipitation. If, to mixtures containing a constant quantity of negative colloid A and increasing proportions of an electrolyte which does not precipitate this colloid, one adds a constant quantity of colloid B, it is noticed that for weak quantities of electrolyte the precipitate is a mixture of A and B, for increasing amounts of electrolyte the precipitate consists of B alone, while for the strongest amounts of electrolyte the precipitate contains a mixture of A and B. The precipitate resulting from the mixture of two colloids of opposed signs can generally be dissociated by the addition of an electrolyte capable of precipitating one of the couples."[1]

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[1] Ashley, U. S. Geol. Surv., *Bull.* **388**, p. 21.

[2] F. P. Hall, "The Effect of Hydrogen Ion Concentration on Clay Suspensions," *Jour. Amer. Ceram. Soc.*, **7** [9], 989 (1923).

[3] Ashley, U. S. Geol. Surv., *Bull.* **388**, p. 20.

Taylor says, with reference to colloids in soils, "Humus...is emulsoid in character...and acts as a protective colloid for suspensoid colloids in the soil." "As a negative colloid, humus is precipitated by kations... It alters the way the soil works."[2] With general reference to protective action Taylor says"...a suspensoid sol when mixed in suitable proportions with an emulsoid sol, loses most of its characteristic properties, and gains those of the protecting emulsoid."[3]

Alexander states that "the effects of vegetable extractive matters on the working properties of clay have been known from ancient times—in the Bible (Exodus V) it is mentioned that brick cannot be made without straw. Recently patents have been taken out for 'Egyptianizing' clay by adding to it tannin, extract of straw, humus and the like. Glue and similar protectives deflocculate or 'free out' clay and make it 'cover' in paper-coating and kalsomining."[4] And further "there are numerous organic substances...which act as protective colloids and tend to produce and maintain the...deflocculated conditions."[5]

The fact that more alkali is required to flocculate natural clay soils than kaolin suspensions has been attributed to the protective action of the humus present.[6]

Acheson improved the properties of certain clays by adding "humus."[7]

Action of Mill Liquor

If the action of electrolytes on the colloidal matter is the basis of the problem, the materials dissolved in the mill liquor cannot be overlooked as to their relation to the colloidal matter in the ground batch or to the electrolyte to be added in setting up.

Suggestive of the nature of mill liquor it may be well to record the results of a test made on the liquid which separated on top of a grind of a relatively insoluble enamel without mill addition. The colloidal matter in suspension in a 100 cc. sample was coagulated by ammonium chloride and filtered off. The filtrate was evaporated to dryness. Determinations on the coagulum and filtrate residue were made.

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[1] Ashley, U. S. Geol. Surv., *Bull.* **388**, p. 31.

[2] Taylor, *op. cit.*, p. 290–91.

[3] *Ibid.*, p. 131.

[4] Alexander, *op. cit.*, p. 42.

[5] *Ibid.*, p. 44.

[6] *Ibid.*, p. 46.

[7] Ashley, U. S. Geol. Surv., *Bull.* **388**, p. 12.

COAGULUM

	Grain
Dried weight	.2624
Ignited weight	.2418
Loss in ignition	.0206
Silica	.1592

= 66.0% of ignited coagulum.

FILTRATE RESIDUE

	Grain
After gentle heating	.4149
Ignited	.3427
Loss on ignition (contained some NH_4Cl)	.0722
Silica	.0251

= 7.3% of ignited filtrate residue.

The high percentage of silica in the coagulum and the low amount in the filtrate residue are worthy of note. There must have been a considerable amount of alkalis and probably B_2O_3 in solution in the mill liquor.

Differences in Enamel

There is no doubt a difference in enamels as related to the action of clay. They may vary in solubility in the mill liquor. Depending on the fineness of grinding, more or less of the enamel substance proper may enter the colloidal state and call for flocculation later.

Applications

With the above or any other theory as the working basis, it becomes necessary to have a correct conception of the physical properties of the enamel slip as a means of making observations experimentally and correlating them with the practical phases of the problem.

E. C. Bingham has suggested[1] that our old habit of working in terms of a viscous liquid is wrong and that we should think of our enamel slip as a plastic solid whose behavior is to be judged in terms of "mobility" and "yield point." This line of reasoning as applied in certain industries has brought most encouraging results. R. D. Cooke has made a preliminary application to our problem and more work along this line may be expected to throw much light.[2]

The purpose of this presentation has not been to proclaim any new ideas or to herald the results of new accomplishments, but to stimulate thought and research of a fundamental nature. It is hoped that a discussion of the ideas presented may be had that will promote the end in view.

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[1] E. C. Bingham, "Discussion on Plasticity," *Bull. Amer. Ceram. Soc.*, **3** [10], 375–79 (1924).

[2] R. D. Cooke, "Plastic Properties of Enamel Slip," *Jour. Amer. Ceram. Soc.*, **7** [9], 651–55(1924).

Among books, in addition to the references given, well worth study are the following:

"Handbook of Colloid Chemistry," Oswald.
"Applied Colloid Chemistry," Bancroft.
"Fluidity and Plasticity," Bingham.
"Laboratory Manual of Colloid Chemistry," Holmes.
"The Chemistry and Physics of Clays and Other Ceramic Materials," Searle.
Transactions, *Journal* and *Bulletin*, AMERICAN CERAMIC SOCIETY.

THE PFAUDLER CO.
ELYRIA, OHIO

LABORATORY EXPERIMENTS IN THE DEVELOPMENT OF A PLANT DRIER[1]

By Wayne E. Barrett

ABSTRACT

Experiments show that the direction of flow of air or other drying media should be parallel to the hollow spaces of hollow tile and drain tile. Its velocity should be approximately 60 feet per minute for maximum safe drying and its humidity may be reasonably low providing the temperature of the clay in the block or tile is high.

Introduction

In firing hollow tile and drain tile, it has been noticed that invariably when they are set wet in the kilns, they will finish drying and firing without cracking. At the same time, excessive cracking will take place in the waste heat drier when the same pieces are completely dried before going into the kilns. Analyzing the results for reasons why this should be, it was found that in the case of drying the tile, in the kilns, which are down-draft, the direction of the drying media was parallel to and through the cells of the block. While on the other hand, in the drier the direction of the drying media was perpendicular to the cells of the tile. Only eddy currents were responsible for the drying within the cells. Furthermore, since the warmest gases are lightest, they will be found at the top and the coldest at the bottom. Since drying will take place most rapidly in the presence of warm air, other things being equal, the tops of the tile dry first causing more or less strain and often cracking.

Procedure

Following the idea gained from the kiln, an experimental section of a drier was constructed as shown in Fig. 1. The idea in mind, was to build a drier that would periodically and automatically deflect the air through the tile as they passed through the drier. The roof and floor for deflecting the air were first built as shown by 1 (Fig. 1).

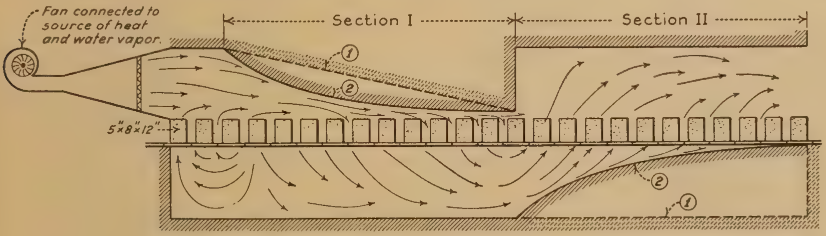

Fig. 1.

Actually drying green tile, it was found that the drying took place at the two ends of each section, the middle of each remaining relatively wet.

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[1] Recd. Feb. 3, 1925. Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb., 1925. (Heavy Clay Products Division.)

A natural conclusion was that through induction, the air was being pulled through the tile in a reverse direction at the left hand end of each section. At the right hand end the air progressed as planned, while in the middle there was no vertical circulation up or down.

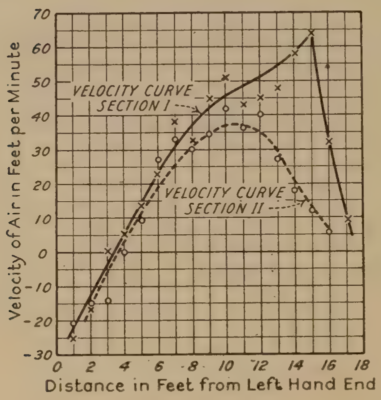

FIG. 2.

Using an anemometer to determine the velocity of the air through the block, the roof and floor were rechanged until they assumed some such position as 2 (Fig. 1). The velocity of the air downward in section I still remained unbalanced (probably due to the closeness of the fan), while the velocity upward in section II was in a relatively balanced condition.

Refilling the drier, the drying was repeated with results somewhat different, particularly in section II. Drying was more uniform from end to end of each section and without cracking. Ninety per cent of the total loss in weight (approximately factory results), occurred in 15 hours. The minimum safe drying time in the plant drier is 48 hours.

However it was noticed in section I that the tops of the tile still dried first. This was probably due to the fact that the air in reaching the right hand end had to pass over the tile in the left hand end. Since the pallets protected the bottom ends of the tile, this did not occur in section II. The air velocities through the tile are shown in Fig. 2.

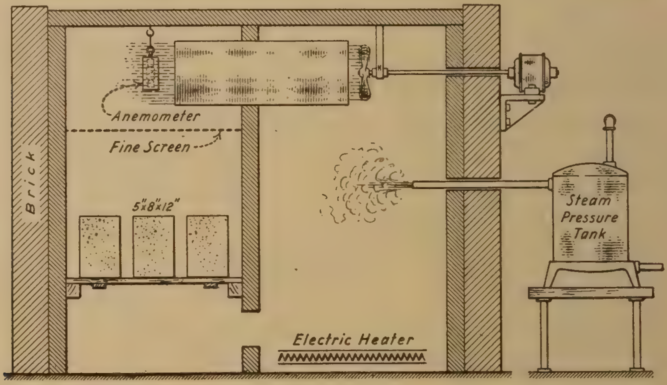

FIG. 3.

Further experimentation to secure an absolute vertical movement of the air and more definite control was then started using the drier and equipment shown in Fig. 3, which is patterned somewhat after the Proctor drier.

In this drier 90% of the total water content was removed in nine hours without cracking the tile.

Results

By noting the curves of Fig. 4, it may be seen that as the humidity starts to drop, the rate of drying naturally begins to increase, and the rate of temperature rise of the tile begins to fall. What is taking place, is that the heat which had been going into the tile to raise its temperature, is now going into the evaporation of the water. A series of attempts to heat the block to a high temperature before starting the drying failed for the reason that the humidity of the surrounding air was too low. (Leakage of the drier prevented raising the humidity.) However, it is believed from these experiments, that had it been possible to raise the temperature of the tile to roughly 175°F that the drying would have taken place in half the time that they were actually dried in, and with disregard to all humidity conditions.

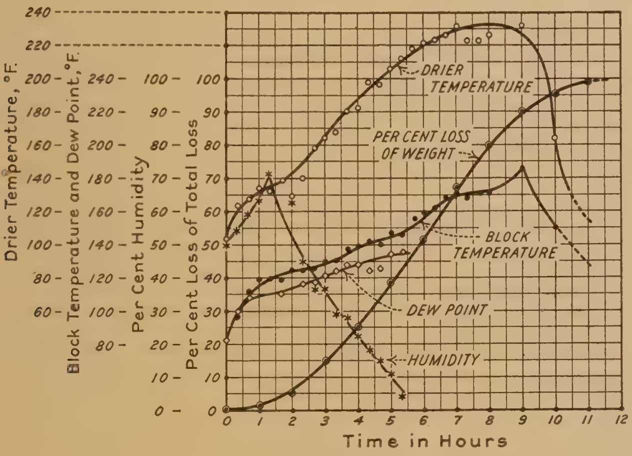

FIG. 4.

In plotting out the curve of the dew point, it was found to be below the temperature of the block, and oddly enough, it was found to be about the same number of degrees below for almost every different rate of raise of temperature in the drier. This would indicate that the drying might have taken place even faster than it did if the humidity had been lowered.

Conclusions

The conclusions to be drawn from these experiments are, that the drying media must travel in a direction that will strike all the surfaces equally and in a positive manner; that the drying may take place very rapidly providing the shrinkage is uniform all over the tile; that the velocity, for maximum safe drying of the air, should not be over 60 feet per minute;[1] that if the tile are heated to a very high temperature, the drying may proceed much more rapidly than if the tile are at a low temperature; that a type of drier that would give a circulation of air through the tile instead of along its sides would speed up drying safely. These things are taken care of in the Proctor type of drier, but due to their great expense and the expense of operation, the type of drier as shown by Fig. 1 would almost as effectively do the work and at a much lower cost of construction and operation.

Adel Clay Products Co.
Adel, Iowa

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[1] This is the velocity that H. D. Tiemann (in charge of the timber physics and kiln drying experiments of the U. S. Forest Service, Forestry Products Lab., Univ. of Wis.) has found to be the maximum safe velocity for drying lumber.

THE PARTICLE ANALYSIS OF CLAYS BY SEDIMENTATION[1]

By Edward Schramm and E. W. Scripture, Jr.

ABSTRACT

As a result of the analysis of Odén, it is possible to apply the sedimentation method quantitatively to the determination of particle distribution of clays in the dispersed state. An experimental procedure is described by which a number of points on the curve may be determined without the aid of any special apparatus. Sedimentation without the aid of a deflocculating agent gives valuable information as to the condition of the clay. Flocculated clays behave like jellies and the method of particle analysis cannot be applied in this case. Data concerning the usual physical properties are presented and these are found consistent with the results of the sedimentation tests as confirmed by microscope observations. The dispersed and fine grained clays are characterized by high dry strength, and the effect of deflocculating a clay is to increase its dry strength.

Introductory

During the past few years there have appeared a number of papers describing the application of sedimentation to the determination of distribution of particle sizes in fine grained materials.[2] These are all based on the work of Sven Odén[3] which was reviewed by Svedberg and Rinde.[2]

According to Stokes' law, $r^2 = \frac{9}{2}\frac{\eta h}{(\Delta - \delta)gt}$ in which r is the radius of a sphere of material of density Δ, which will fall through a height h in time t in a liquid of density δ and viscosity η. For water at 20° we may take $\delta = 1$, $\eta = .01$. With h in cm., t in seconds, $g = 980$, we calculate r in cm. If we have a clay suspension containing particles of all sizes falling through all heights from zero to some definite value, the rate of accumulation of sediment will evidently depend on the distribution of particle sizes. Odén analyzed this case, showing that if we express the amount of material settling as percentage of the total originally in suspension, the result for a given time and height of column is independent of the strength of the suspension; furthermore, if the results with different heights of column are corrected to a unit basis (a proportionate correction being made in the time) the results are independent of the actual height of the column. Odén weighed the amount of sediment accumulating on a plate suspended on a balance, adding small counterweights to maintain the balance equilibrium. He derived the relation

$$\frac{dS}{dr} = -\frac{2t^2}{r}\frac{d^2P}{dt^2}$$

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb., 1925. (White Ware Division.)

[2] Schurecht, *Jour. Amer. Ceramic Soc.*, **4**, 812 (1922); Svedberg and Rinde, *Jour. Amer. Chem. Soc.*, **45**, 943 (1923); W. J. Kelly, *Ind. Eng. Chem.*, **16**, 928 (1924); Kraemer and Stamm, *Jour. Amer. Chem. Soc.*, **46**, 2709 (1924).

[3] Odén, *Proc. Roy. Soc. Edinburgh*, **36**, 219 (1916).

where dS is the percentage mass of particles corresponding to the radius interval dr, t is the time of fall, and P the total percentage weight of sediment corresponding to the time t. r may be calculated from Stokes' law for the time t. Svedberg and Rinde[1] showed that the values $\frac{dS}{dr}$ can be obtained by a simple graphical method. The percentage weight of sediment, P, is plotted as ordinate against the time, t, as abscissa. If we draw tangents to the curve at points corresponding to the time t_1 and t_2, the difference between the intercepts on the weight axis gives directly the percentage of material of sizes between r_1 and r_2 as calculated from Stokes' law for the times t_1 and t_2 (see Fig. 1).

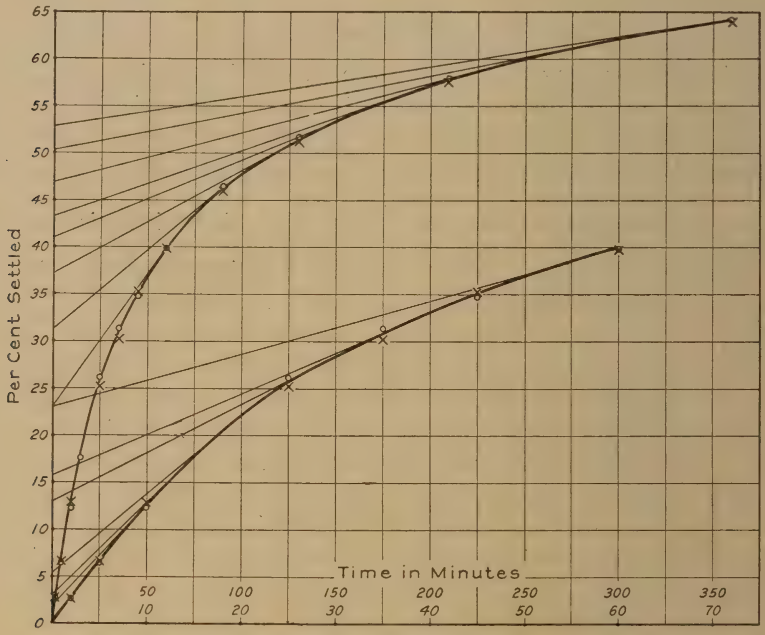

FIG. 1.—Clay No. 2.

The correctness of this method of analysis depends on the validity of Stokes' law which is strictly true only for spherical particles. In considering particles of various shapes, Odén found it convenient to define r as the mean effective radius, *i. e.*, the radius of a sphere which will have the same time of fall as the particle in question. The greater the proportion of flat or flaky particles, the more uncertain will be the results, but the method will nevertheless give a valuable approximation which is all that can be achieved by any known procedure, and as will be shown below, can be carried out experimentally with no special apparatus of any kind. To give some idea of the degree of accuracy Odén gives the following comparison for a sample of Swedish soil:

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[1] *Loc. cit.*

r (μ)	r' (μ)
78	100
24.8	30
8.3	10
2.9	3
1.03	1

In the above r is the mean effective radius calculated according to Stokes' law and r' the mean radius according to microscope measurements by Atterberg.

Svedberg and Rinde refined Odén's method by substituting for the addition of counterweights an electrical method of maintaining the balance which enabled them to work with smaller quantities of material and investigate colloidal metals. Kelly made use of the change in density as settling proceeded, measuring this by the recession of liquid in a capillary side tube. All of these methods are continuous, giving a great number of points on the accumulation curve. It appeared to us that the general procedure offered promise as a means of studying the structure of clays, more especially of the ball clays and refined kaolins. By contenting ourselves with the determination of a dozen points which are ample to define the curve accurately within the practicable working range, we were able to secure the data with a set of test-tubes and a wooden rack.

Experimental

The procedure adopted was as follows: We selected one dozen test-tubes of Pyrex glass 300 mm. long, 32 mm. outside diameter and of as uniform bore as possible. Exactly 20 cc. of water was introduced into each tube and the position of the meniscus marked with a label. A second mark was made on the tubes at a definite height (221 mm.) above the first. The volume between the marks was then determined by running in water. We now had a fixed height between the marks, a fixed volume below the lower mark, and a known total volume for each tube. To determine the accumulation curve the tubes were placed in two rows in a wooden rack designed to hold them vertical, filled with clay slip and shaken together. At stated intervals, the suspension was siphoned off down to the lower mark, the residue transferred to a weighed dish, evaporated to dryness and weighed. While the tubes are being filled the slip is kept in agitation by a motor driven stirrer. A portion of slip is also siphoned into a graduated flask and this is evaporated down for the determination of the strength of suspension in each experiment. Knowing the concentration we can calculate the weight of clay between the marks in each tube and the weight below the lower label in all the tubes; the latter is subtracted from the weight of residue to give the weight of clay which has settled from the column between the marks. It is sometimes difficult to fill and draw the tubes accurately to the mark with a siphon and the final adjustment may be made with a pipette. Since the viscosity of water varies with temperature it is important to keep the latter as nearly constant as possible.

Needless to say, if we are to get a true picture of the distribution of particles the sample of clay must be completely deflocculated. The behavior of flocculated and deflocculated clays on sedimentation differs not only in degree but also in kind. The flocculated clays are gelatinous and settle like a mass of jelly; the particles or groups of particles do not fall freely in a viscous medium and Stokes' law is inapplicable. The volume of jelly-like sediment after settling is proportional to the degree of flocculation. With deflocculated clays the particles fall freely and the sediment is dense in character. The direct sedimentation of clays with distilled water is therefore valuable chiefly as a qualitative test for dispersion and can tell us nothing about the size of the ultimate particles. Some experimental observations bearing on this point will be presented later.

Water glass (of the composition $Na_2O.2.8SiO_2$) was used as a deflocculating agent because of the wide range of concentrations in which maximum effect may be obtained with different clays. As a result of preliminary experiments it was found that a proportion of 0.75% $Na_2O.2.8SiO_2$ of the weight of clay gave best results with a number of clays and this ratio was adopted as standard.

Specific gravity determinations on nine clays gave an average figure of 2.632 which was used in calculations from Stokes' law.

The usual procedure was to crush the clay in a mortar, make up a 5%

Table I

China Clay No. 1				China Clay No. 2			
Time, min.	Per cent settled	Time, min.	Per cent settled	Time, min.	Per cent settled	Time, min.	Per cent settled
2	4.3	2	4.1	2	2.68	2	2.74
5	7.8	5	7.1	5	6.43	5	6.66
10	12.4	10	12.4	10	12.3	10	12.9
15	17.0	20	21.0	15	17.6	15	...
25	22.8	30	26.6	25	26.2	25	25.2
35	28.9	..	..	35	31.4	35	30.2
45	34.0	45	32.5	45	34.8	45	35.3
60	36.4	60	36.6	60	39.9	60	39.8
90	43.3	90	43.0	90	46.5	90	46.0
130	49.3	130	48.7	130	51.7	130	51.2
210	56.4	210	55.6	210	58.0	210	57.7
..	..	360	61.8	360	64.3	360	64.1

suspension with the proper addition of water glass, blunge one hour, let stand over night and reblunge in the morning before filling the tubes. In the case of ball clays the slip was passed through a fine screen to remove coarse organic matter before sampling. The clays investigated comprised 7 English china clays, 1 English ball clay, 1 Tennessee ball clay, 1 Florida secondary kaolin, 1 North Carolina specially refined primary kaolin.

To show the reproducibility of results we give in Table I and in the curve data from separate runs on two English china clays.

To show the validity of using a 5% suspension, we give in Table II a comparison of results obtained with 1% and 5% suspensions. Working with 1% suspensions, weighings are made to 1 mg., with 5% to 10 mg.

TABLE II

China Clay No. 3

Time, min.	Per cent settled	
	1% susp.	5% susp.
2	4.15	3.72
5	10.6	8.5
10	18.1	16.0
15	24.7	23.0
25	33.4	31.3
35	38.9	37.0
45	45.0	42.5
60	48.6	47.5
90	55.2	54.2
130	60.9	60.2
210	67.8	67.1
360	72.2	73.3

The data for the remainder of the clays are given in Table III.

TABLE III

Per Cent Settled

Time, min.	English China Clays				Eng. ball	Tenn. ball	Fla.	N. Car.
	No. 4	No. 5	No. 6	No. 7				
2	2.9	1.47	2.15	2.54	2.56	0.55	6.14	0.4
5	6.7	4.0	4.85	5.75	5.66	0.83	11.3	1.34
10	12.1	7.9	9.8	11.0	9.32	2.05	17.5	3.3
15	16.4	11.4	13.0	15.0	11.3	3.28	22.1	4.9
25	22.4	16.7	18.8	20.9	14.4	5.00	28.1	8.6
35	27.5	21.6	22.7	25.1	15.9	7.44	31.2	11.6
45	30.5	25.0	26.3	27.8	18.6	8.88	35.6	14.3
60	33.6	28.2	29.4	31.5	20.0	11.2	38.8	17.1
90	39.9	33.9	34.5	36.1	23.3	15.1	44.0	22.6
130	45.4	38.2	38.8	40.5	26.1	20.1	48.0	27.2
210	53.2	46.0	44.8	46.4	30.9	26.6	53.3	33.4
360	57.6	52.5	51.4	53.2	35.4	33.5	59.1	39.6

TABLE IV
DISTRIBUTION OF PARTICLE SIZES

Time, min.	Range of sizes radius μ			English China Clays Per cent							Per cent			
				No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	Eng. ball	Tenn. ball	Fla.	N. Car.
5	>	14.3		2.1	0.3	0.4	0.5	0.1	0.3	0.5	1.2	0.0	4.4	0.0
10	14.3	to	10.3	0.7	1.5	1.6	2.1	0.5	0.9	1.2	2.8	0.0	2.2	0.0
15	10.3	to	8.3	1.8	1.2	6.0	2.4	1.1	1.3	2.1	2.3	0.0	3.4	0.0
20	8.3	to	7.2	2.2	2.3	2.8	1.7	1.9	2.5	2.5	1.1	0.0	3.3	0.0
30	7.2	to	5.9	3.6	7.7	4.1	4.1	1.6	3.6	4.9	1.2	0.0	4.4	0.9
40	5.9	to	5.1	5.4	2.7	4.2	6.4	3.8	2.2	2.2	0.6	1.3	2.7	1.7
60	5.1	to	4.1	7.2	7.3	12.5	3.2	7.2	6.6	6.2	3.5	1.1	4.6	2.4
90	4.1	to	3.2	3.5	8.2	5.0	2.1	3.5	3.8	4.8	2.6	1.0	7.5	4.6
130	3.2	to	2.8	6.7	6.0	7.9	4.4	4.3	5.3	3.8	1.7	2.6	4.6	5.3
160	2.8	to	2.5	4.3	3.8	4.7	3.5	2.0	2.2	2.8	1.2	3.6	2.2	1.7
200	2.5	to	2.3	3.5	2.2	2.9	6.6	3.6	2.9	1.8	2.1	3.7	1.9	2.2
250	2.3	to	2.0	4.8	3.6	4.2	7.0	5.6	2.1	2.5	3.7	1.9	3.4	4.5
300	2.0	to	1.85	4.0	3.6	4.0	3.2	5.0	3.8	3.6	2.4	2.8	2.9	3.5
350	1.85	to	1.7	2.0	2.4	3.1	3.3	2.3	3.4	3.1	1.6	2.8	2.7	4.0
	<	1.7		48.2	47.2	36.6	48.5	57.5	59.1	58.0	72.0	79.2	49.8	69.2

These percentages were plotted against time and tangents drawn to obtain the distribution of particles as previously described. A typical curve is given. The first part of the curve was plotted on a more open time scale to enable the tangents to be drawn more accurately. The distribution figures are given in Table IV.

It will be obvious that of the particles remaining in suspension at any time none should exceed the radius calculated from Stokes' law for that time. This affords a rough method of checking with the microscope the correctness of the results. Slides were prepared from the siphoned-off suspensions by the method described by Weigel.[1]

About a dozen of the largest grains in each slide were measured with the aid of an eye-piece grating. The result for Clay No. 1 expressed in μ was as follows:

r (observed)	18.2	15.6	12.0	9.7	7.8	7.0	6.0	3.9	3.6	2.6
r (calcd.)	22.8	14.3	10.3	7.2	5.9	5.1	4.1	2.8	2.3	1.7

The observed diameters are generally greater than the calculated. This is to be expected since with the microscope we are measuring the maximum rather than the mean radius of the particles.

It was early observed that if the deflocculating agent were omitted and if the clay was naturally flocculated, the suspension settled as a jelly leaving clear liquid above. If we attempt to apply the method of analysis herein described to such a system, we get an anomalous result; the rate of settling at the start is *slower* than with a dispersed system although in the latter case we do not get a clear liquid for long periods of time. If the floccules were falling freely as individuals, we should, of course, have a very much faster rate of settling. However, the sedimentation of the clay in its natural state in distilled water gives valuable information to supplement the particle analysis. A series of observations on the clays here investigated is given in Table V.

TABLE V

UNTREATED CLAY SUSPENSIONS

Clay No.	Division between liquid and suspension	State of liquid	State of sediment	General
1	Sharp	Very clear	Loose and bulky	Flocculent
2	Sharp	Fairly clear	Loose and bulky	Flocculent like No. 1 but liquid slightly turbid
3	Sharp	Perfectly clear	Loose and bulky	Flocculent
4	Indistinct	Very turbid	Very compact	Dispersed

---

[1] W. M. Weigel, "Size and Character of Grains of Nonmetallic Mineral Fillers," Bur. of Mines, *Tech. Paper* 296.

TABLE V (*Continued*)

Clay No.	Division between liquid and suspension	State of liquid	State of sediment	General
5	Sharp	Fairly clear	Loose and bulky	Flocculent
6	Indistinct	Very turbid	Compact	Dispersed
7	Sharp	Very clear	Loose and bulky	Flocculent
Eng. ball	Indistinct	Very turbid	Very compact	Completely dispersed
Florida	Sharp	Fairly turbid	Somewhat compact	Characteristics of both flocculent and dispersed clays; former predominating
N. Car.	Indistinct	Very turbid	Somewhat compact	Partially dispersed; loose sediment, turbid liquid
Tenn. ball	Indistinct	Very turbid	Very compact	Completely dispersed

The above observations as to the nature of the clays were confirmed by the microscope. The flocculent and dispersed clays appeared in marked contrast, and clays like the Florida and North Carolina showed flocculated masses and dispersed fine particles.

We shall now present in tabular form a summary of the properties of the different clays:

TABLE VI

Clay No.	State of aggregation	% below 1.7 μ
1	Flocculent	48.2
2	Flocculent	47.2
3	Flocculent	36.6
4	Dispersed	48.5
5	Flocculent	57.5
6	Dispersed	59.1
7	Flocculent	58.0
Eng. ball.	Dispersed	72.0
Florida	Partly dispersed	49.8
N. Car.	Partly dispersed	69.2
Tenn. ball	Dispersed	79.2

It will be noted that the china clays may be of coarser or finer grain and either variety may be flocculent or dispersed. The ball clays, both English and American, are of very fine grain and completely dispersed. The secondary and primary American kaolins may be of coarse or fine grain and have some of the properties of both flocculated and deflocculated clays.

It will now be of interest to present data on other properties of these clays which may be interpreted in the light of the foregoing.

TABLE VII

PROPERTIES OF CLAYS

Clay No.	Fired cone	Per cent linear shrink.		Per cent absorp.	Per cent water of plasticity	Mod. of rupture	
		Drying	Total			Dry	Fired
1	11 started	2.08	7.28	23.4	30.8	57	2450
2	11 started	2.18	6.82	24.3	29.0	59	....
3	11 started	1.54	6.25	25.1	29.1	39	1710
4	11 started	3.09	10.62	19.0	34.3	180	3960
5	11 started	1.31	6.25	23.8	29.1	62	3090
6	11 started	2.56	9.90	18.4	..	194	4005
7	11 started	1.67	7.93	21.4	..	104	3990
Eng. ball	10 half over	5.5	15.3	0.0	..	452	5845
Florida	11 half over	7.0	16.6	13.8	..	242	6420
N. Car.	10 3/4 over	3.8	11.0	17.0	32.1	311	5170
Tenn. ball	10 3/4 over	4.0	11.1	0.0	..	385	8130

Considering the English china clays, it will be noted that Clay No. 3, which is coarse and flocculated, possesses the lowest shrinkage, highest absorption, low water of plasticity, and the lowest dry and fired strength. Clay No. 6, possessing the lowest absorption and highest dry and fired strength, is fine grained and dispersed. It is followed closely by No. 4, which is also dispersed, but of somewhat coarser grain. Of the remaining china clays which are all flocculated, No. 7, having the finest grain, shows the lowest absorption and highest dry strength. Nos. 1, 2, and 5 are intermediate in characteristics. Similar relations hold for the other clays. The ball clays, of very fine grain and completely dispersed, exhibit the highest shrinkage and dry strength.

These relationships are in conformity with the known plastic or working qualities of the clays. Both the plastic and the dry strength are affected by the distribution of particle sizes and the state of aggregation of the clay. The fired strength is probably also influenced by the same factors, though the case here is not so simple since the question of flux content enters.

If the views presented herein are correct, the deflocculation of a clay should result in increased dry strength. This has been proven by Schurecht,[1] who says: "The increase in mechanical strength may be largely due to the fact that the finer grains would pack more closely and hence make a denser body." To verify Schurecht's observations, china clays Nos. 1 and 7 were treated with the usual amount of water glass, brought to a plastic condition and made into briquettes. The dry strength of No. 1 was increased by the treatment from 57 to 80, of No. 7 from 104 to 185. The greater increase with No. 7 is due to the greater fineness of the ultimate particles and the treatment has brought it in the class of Nos. 4 and 6 which are initially deflocculated.

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[1] H. G. Schurecht, "The Use of Electrolytes in the Purification and Preparation of Clays," Bur. of Mines, *Tech. Paper* **281** (1922).

Obviously the rate of drying will depend on the physical structure of the clay. We determined this rate for four china clays under arbitrary conditions; the clays were brought to a similar plastic condition and made into small briquettes which were placed in an oven and removed after one hour at 35°C, one hour at 50°, one hour at 60°, and heating to constant weight at 110°. The clays so studied were a relatively coarse grained flocculent clay (No. 2); a fine grained flocculent clay (No. 7); a relatively coarse grained dispersed clay (No. 4); a fine grained, dispersed clay (No. 6). The results are given in Table VIII.

TABLE VIII

DRYING BEHAVIOR

Clay	Per Cent Loss in Weight 1 hr. at 35°	1 hr. at 50°	1 hr. at 60°	Constant weight
2	4.8	12.3	23.6	25.7
7	4.2	10.8	22.0	26.5
4	4.3	11.7	22.5	30.6
6	4.0	10.6	23.0	29.7

The clays of finest grain (7 and 6) have the slowest initial drying rate, while the dispersed clays (4 and 6) have the highest water of plasticity.

Summary

As a result of the analysis of Odén, it is possible to apply the sedimentation method quantitatively to the determination of particle distribution of clays in the dispersed state. An experimental procedure is described by which a number of points on the curve may be determined without the aid of any special apparatus. Sedimentation without the aid of a deflocculating agent gives valuable information as to the condition of the clay. Flocculated clays behave like jellies and the method of particle analysis cannot be applied in this case. Data concerning the usual physical properties are presented and these are found consistent with the results of the sedimentation tests as confirmed by microscope observations. The dispersed and fine grained clays are characterized by high dry strength, and the effect of deflocculating a clay is to increase its dry strength.

ONONDAGA POTTERY CO. LABORATORY
SYRACUSE, N. Y.

AMERICAN CLAYS AS COMPARED TO ENGLISH CLAYS IN WHITE WARE BODIES[1]

By E. H. Fritz

ABSTRACT

A summary of the discussion at Atlantic City on this subject is given, bringing out Dr. Langenbeck's charge that the failure to make wider use of American clays is due to the ceramic profession, which has not given American clay producers specific information as to requirements which must be met in order to compete with English clays.

This charge is refuted, because such information is available and various tests which are made are enumerated. The charge is made that many clay producers either do not know how, or, are not sufficiently interested to make use of such information when it is given them.

Comparative results with English and American clays are given in regard to general uniformity, plasticity, bonding strength and vitrification. Equal or better results were obtained with the American clays in every case except vitrification temperature of the ball clays which was somewhat higher.

A body was developed from the best American clays which equaled any of the English clay bodies, the difference in vitrification temperature of the ball clays apparently having no adverse effect at a firing temperature of cone 10. The results are based on commercial use.

It is concluded that English clays can be eliminated in most white ware bodies.

At the Atlantic City Meeting, a year ago, a very interesting discussion[2] was led by Dr. Langenbeck on "What has been the experience in substituting domestic secondary and primary kaolins for English china clays?" and ball clays were also included by his consent. The consensus of opinion of those taking part was:

1. While the uniformity of all clays cannot be guaranteed, English clays will average more uniform than the American.
2. English ball clays have a lower vitrification temperature than the American.
3. English clays have better plasticity and greater bonding strength.
4. Better color can be expected from the English material, especially china clays.

The discussion also brought out two cases of successful substitution of American clays for the English. No specific information was given as to the kind of tests which had been used upon which such substitution had been based, nor did any one else who was attempting to substitute American clays give any information as to the kind of tests employed. As a result, Dr. Langenbeck, charged the apparent failure to make wider use of American clays, to the ceramic profession, for, he claimed, that the American producers had been given no definite information as to what requirements they had to meet in order to compete with the English clays.

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb., 1925. (White Ware Division.)

[2] *Bull. Amer. Ceram. Soc.*, **3** [11], 417–34 (1925).

We were one of the two cases of successful substitution, making use of American clays in our dry press electrical porcelain work, which we have been doing for some time. The failure of myself and the others to give information as to the tests employed, was, I am sure, not due to not having any, for I believe, all of us make use of the same simple tests which have been in use for some time. At our plant we determine the water of plasticity, rate of slaking, amount of residue on 150-mesh lawn, modulus of rupture in the unfired state, dry shrinkage, firing shrinkage and vitrification which is determined by the per cent of absorption at cone 10. This is our preliminary test, and, if the results are within the limits specified for each property, we substitute the clay for a similar clay in our regular body mix, making up about six hundred pounds of this body with laboratory equipment. This equipment duplicates as closely as possible the equipment used in the factory. From this body we make up standard insulators, having them made by men in the factory who are capable of giving an accurate opinion as to how this body compares with the regular body mix. We consider this a very important test, especially as to plasticity and workability. If the results of this trial are satisfactory, we purchase a carload of the clay and use it in the factory in the regular way; keeping accurate records of manufacturing losses and finally test the quality of the finished product. This constitutes the final test. This method of testing is not as accurate as I would like to see it, for it is quite possible that a clay will pass the preliminary tests and then fail on the final factory trial on account of higher losses. It is often impossible to find the reason for this and in such a case we cannot tell the producer why his clay is not satisfactory. It is, however, the best that is available for our purpose at the present time.

The test for plasticity, upon which we depend, is especially crude and has been condemned by some writers; but I find that although it is apt to be inaccurate at times, it is by far the most dependable test that we have ever used. We have been doing considerable work during the past year on the Bingham plastometer method of determining plasticity. This shows considerable promise and we hope to be able to apply this test in a routine way before long.

I am not in agreement with Dr. Langenbeck, therefore, in his deduction that lack of progress in testing clays has prevented free competition between English and American clays, for comparable data on many similar clays is available to the producers. Regardless of the nature of the tests employed, however, it is extremely doubtful to me, that such data would be of any assistance to most of the clay producers in meeting the requirements. I have often told producers what type of clay we wanted, in terms of test results, and instead of telling me that they did or did not have such a clay, in most cases their answer is "Test ours and see if it will do." I am reminded of another case where a ball clay became variable in vitrification. Upon bringing this to the attention of the producer the reply was that they were selecting the clay according to a fixed standard which was based on appearance, and beyond this they could not guarantee it free of variation. In other words, they could not control vitrification and were not sufficiently interested to investigate this variation.

Since the time of the last Meeting we have done considerable work on the substitution of American for English clays in our plastic process body. Our results with the English clays showed:

1. Some ball clays are exceedingly variable especially in plasticity. This was indicated by the great variation in the amount of water necessary to blunge the body in which such clays were used. This variation was as high as 100%; that is, the maximum was twice the minimum amount of water used. There was naturally a difference in the workability of this material in the plastic form, which, of course, is disastrous for manufacturing operations.
2. The china clays as a class are weaker and less plastic than a good standard Georgia kaolin. They were more apt to tear under the trimming wire, causing higher drying and firing losses.
3. Some of the English clays, especially some ball clays, gave us more trouble on account of their individual variations, than we ever had with any American clay.

With American clays we found similar variations in the ball clays as were found with the English clays, but they were not as great. This leads me to believe that American miners who know their business and have an established reputation, are more selective with their clays than English miners. Successive carloads of some English clays were so different in appearance, that I am quite sure the American miner would never have thought of shipping it under the same name, at least, I have never seen American clay come in that way. My opinion, therefore, in regard to comparative uniformity has been changed and I believe now that the advantage in this respect lies with the American clays.

Regarding plasticity and bonding strength, as just mentioned we found English china clays inferior to the best Georgia clays. English ball clays average better than the American in these properties, but we did find a few Tennessee and Kentucky balls, which, when used in combinations, were equal to the best English balls.

We were still not able to find any American ball clay whose vitrification temperature was as low as that of most English balls. The nearest result obtained was cone 9, which is considerably higher than that of most any English. In color there was no apparent difference between the two classes when fired in body mixes. This is not a true comparison, however, for we did not use the whitest burning English clays, because this property is not essential in our work. There is no doubt but that there are some English china clays which are superior to any others in color.

In only one respect then, vitrification, were we unable to equal the English clays. This difference, however, had no effect in the body in which the best American clays were substituted for English. This is probably due to the fact that at our firing temperature of cone 10, the ball clay would be vitrified anyway. However, if any difference would result in the firing behavior of the body, it should be possible to adjust it by means of a slight increase in the feldspar content.

A body was thus developed in which American clays only were used, and which gave equal results to the best of the English clay type, not only from the standpoint of manufacturing losses, but also, and what is more important, from the standpoint of quality as shown by tests of the finished product. My conclusion, therefore, is that English clays can be eliminated in most white ware bodies since ours is close to the general type of this class. This deduction is not as yet based on extensive use, but we have made a factory trial of the body which I spoke of which extended over a period of several weeks. As a result of this I am satisfied that the substitution can be successfully made. This means that we are placing some American clays on a competitive basis with English, and they have the added advantage in that a more intimate contact can be maintained with the producers on account of their proximity.

WESTINGHOUSE HIGH VOLTAGE INSULATOR CO.
DERRY, PA.

FINE STONEWARE FROM FLINT CLAY

BY PAUL E. COX

ABSTRACT

Based on an observation by Karl Langenbeck[1] in his "Chemistry of Pottery" a fine and very dense stoneware fired at cone 9 has been developed with a Missouri flint clay as the principal raw material. The resulting product is non-absorbing, tough, and a very satisfactory body for ball mill jars, fine art stoneware, and any work where such a body is desired. Plasticity is equal to that of any standard that may be chosen and the body mixture can readily be thrown on the potter's wheel. Control of plasticity can readily be had so that such a body is available for use by any process. The color when fired is that of a poor grade of hard porcelain.

Introduction

Karl Langenbeck, in his "Chemistry of Pottery" says that yellow ware could be made from flint clays, provided wet grinding was done in the preparation of the clay. This idea has been put to a practical test with very satisfactory results, though a yellow body did not result.

The body composition is as follows:

The Flint Clay The flint clay is one from Mokane, Missouri. Its deformation point is cone 34. Its analysis is as follows:

SiO_2	43.71	MgO	0.56
Al_2O_3	39.63	Alkalis	.35
Fe_2O_3	1.27	Ignition loss	14.08
CaO	.40		
			100.00

This was prepared by reducing to dust in the laboratory wet pan, after which the body was prepared by wet grinding in ball mills, and by drying out to a workable condition on plaster.

The Body

The body composition is as follows:

Mokane flint clay	60
Kentucky ball clay	19
Feldspar	14
Bell Fourche, S. D. bentonite	7
	100

The first trials were made without the bentonite but proved impossible to form by the throwing process and the body cracked badly in plaster molds. After the bentonite was added, no trial was made in plaster molds, though there is no possibility that the body will not be possible to work in any desired manner. The thought was that the Kentucky ball clay would suffice for plasticity, following Langenbeck's suggestion to the effect that wet ground flint clays would become very plastic. In this case there was little plasticity in the flint clay. In fire brick practice, however, this flint clay will develop sufficient bonding power to bond itself in brick manufacture.

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[1] Karl Langenbeck, "Chemistry of Pottery," p. 68.

Properties of the Body In the clay state this body works ideally. Vase forms are readily thrown from it, and can be drawn thin enough on the wheel so that finishing of the foot is all the additional work needed. Ball mill jars holding about a gallon were readily made by the stoneware potter's method on the wheel. The fired body is almost as white as many coarse porcelains, gray white in color, very dense, so dense that ink will not pentrate and the body matures at cone 9. The best biscuit temperature where a soft biscuit is desired is at cone 06. Used in ball mills, the body is entirely satisfactory in every way, and could readily be formed into large sized jars. The body was ground to pass a 100-mesh sieve.

Glazed Wares from the Body A vase made from the body, was glazed in a mixture of the following composition:

$$\left.\begin{array}{ll} K_2O & .30 \\ CaO & .35 \\ ZnO & .35 \end{array}\right\} \quad Al_2O_3 \quad .40 \quad \left\{ \quad SiO_2 \quad 4.50 \right.$$

This was stained with 10% of a blue stain such as is commonly sold for use as an underglaze color. This glaze proved a little too stiff and probably would be good if the silica content was reduced to 3.50. No crazing was manifest and the fitting of a glaze would not be at all difficult.

Conclusions

Flint clays will make first rate raw materials for use in fine art stonewares of the type produced by the European governmental porcelain factories, for ball mill jars and similar ball mill fittings, for floor tiles of the type used in mosaic floors, and for certain types of electrical insulators. Such bodies seem particularly fool proof in handling in the plant, because they form easily and are easily adjusted for several processes of manufacture and are easily fitted with glazes.

Acknowledgment Credit is hereby accorded D. A. Moulton for the analysis, deformation point determination, and helpful suggestions about fire brick practice in the use of such clays.

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ORIGINAL PAPERS

THE THERMAL CONDUCTIVITY OF CARBORUNDUM REFRACTORIES[1]

BY M. L. HARTMANN[2] AND O. B. WESTMONT[3]

ABSTRACT

Thermal conductivity measurements up to 1350°C of silicon carbide refractory materials have been made, using the water calorimeter method. Data were secured on furnace walls such as those commonly used in practice and results are believed to be accurate to within about 1%. Conductivity measurements were made on seven carborundum single walls and on eight carborundum-fire-clay composite walls. The relation of the thermal conductivity to temperature, chemical composition, and porosity was investigated, as well as the magnitude of the surface and joint effects. The conductivity of carborundum was found to vary with the quantity of heat energy transmitted through the wall. Tables are given showing the coefficients of thermal conductivity and heat flow through various types of walls with a temperature of 1500°C in the combustion chamber.

Temperature gradient charts and heat flow curves for various walls are also given together with the practical application of the results in the design of commercial furnaces.

Introduction

Conductivity of Silicon Carbide Refractories

Of all the refractory materials available commercially, there are none which even approach silicon carbide or carborundum in its ability to readily transmit heat and at the same time have mechanical strength and chemical inertness to resist the various destructive forces in modern industrial furnaces. The great mechanical strength of commercial refractories made from carborundum has been previously studied.[1] Accurate information concerning their ability to transfer heat under actual operating conditions has been lacking.

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[1] Received Jan. 8, 1925. This paper was presented at the Annual Meeting of the AMERICAN CERAMIC SOCIETY, Columbus, Ohio, February, 1925.

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A number of investigators have studied the thermal conductivity of refractory materials, but insofar as silicon carbide refractories are concerned the results are not concordant, nor has the investigated range of temperatures been sufficiently high. The variation in the published results is perhaps due not only to the difference in the methods used, but also to the differences in the firing temperature, porosity, and chemical composition of the refractories tested.

The thermal conductivity of silicon carbide refractories at low temperatures recorded by Wologdine[2] agrees with the data published several times by The Carborundum Company.[3] These data, however, are quite different from those published recently by Beecher.[4] The results of Watts and King[5] are relative and cannot be compared directly with the values of other investigators. The curve published by M. L. Hartmann[6] represents values secured during the preliminary experimental work recorded herein.

The remarkable increase in the use of carborundum refractories in furnaces requiring a transfer of thermal energy through partition walls makes it desirable to determine accurately not only the relation of the thermal conductivity to temperature, but also its relation to the composition and to the porosity.

Application of Fourier's Law

In many installations, carborundum refractories are insulated so as to prevent rapid heat flow, with the result that the temperature gradient is relatively small. In calculating heat balances in such furnaces, it has been assumed by Fourier's law that the thermal conductivity of the refractory is independent of the temperature gradient and that the heat flow through the composite walls is inversely proportional to the thermal resistivity of each wall.

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[1] Hartmann and Hougen, *Amer. Electrochem. Soc.*, **37**, 707 (1920); Hartmann and Kobler, *ibid.*, **37**, 717 (1920); Hartmann and Koehler, *ibid.*, **40**, 457 (1921).

[2] Wologdine, *Electrochem. and Met. Ind.*, **7**, 383 (1909).

[3] Linbarger, *Chem. and Met. Eng.*, **19**, 489 (1918); *Circular*, The Carborundum Co. (1921).

[4] Beecher, *Jour. Amer. Ceram. Soc.*, **7** [1], 19 (1924).

[5] Watts and King, *Jour. Amer. Ceram. Soc.*, **6** [10], 1075 (1923).

[6] Hartmann, "Refractories for Electric Furnaces," Booklet, The American Electrochem. Soc., p. 69 (1924).

There appears to have been very little experimental work published to determine if the thermal conductivity at a given temperature is a constant regardless of the quantity of energy being transferred. According to the Bureau of Mines Report,[1] the question of the variation of thermal conductivity with different temperature gradients has been raised by E. B. Wilson, recently of the Department of Physics of the Massachusetts Institute of Technology. Fourier's law $\left(Q = k\,\frac{A(t_1 - t_2)}{L}\right)$[2] assumes that the conductivity k, while of course different at different temperatures, is strictly a constant for all values of the temperature gradient $\frac{(t_1 - t_2)}{L}$. Prof. Wilson has pointed out that there is a possibility that this law of heat conduction may not be exactly realized when large temperature gradients are involved.

In single carborundum walls the transferred heat energy is much greater than in the more usual refractory materials, and hence, it seemed desirable to determine whether or not Fourier's law does hold under these unusual conditions. To do this it was necessary to test several composite walls in which the heat flow was decreased by insulation.

Method of Measuring Thermal Conductivity

The most practicable method of measuring the thermal conductivity of refractories under conditions approaching those in practice is the method used by Boyd Dudley, Jr.[3] This method does not require the use of special shapes which may have different thermal properties from those of the commercial brick. The wall under test was built of standard $2^1/_2$ x $4^1/_2$ x 9-inch brick laid up with cement of the same composition as the brick.

The heat transmitted through a definite area of this wall was measured by a waterflow calorimeter eight inches square fitted with a two-inch guard ring. This guard ring prevents lateral flow of heat. The temperature gradient through the wall was measured by thermocouples inserted to various depths in holes bored to within $^1/_4$ inch of the inner face.

For the determination of the thermal conductivity up to 1400°C, it was found that the two-inch guard ring used by Dudley did not insure normal flow of heat through that section of the wall under test. (The highest temperatures obtained by Dudley were not over 1000°C.) For this reason, an additional guard ring was used in our apparatus for the high temperature tests.

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[1] Hersey and Butzler, "Report of Investigations," Ser. No. 2564, Jan., 1924.

[2] Throughout this paper Q = heat flow, k = thermal conductivity, A = area, L = thickness, $t_1 - t_2$ = temperature drop.

[3] Dudley, *Jour. Amer. Electrochem. Soc.*, **27**, 285 (1915).

Experimental Determinations

Apparatus

The furnace used for the conductivity tests is shown in Figs. 1 and 2. This furnace was larger than required so a partition wall was built in the center and only the portion near the test wall was used. One large oil burner operated with 6.6 lbs. air pressure was used to heat this portion of the furnace. A checkerwork was made with carborundum brick as shown so that the oil flame passed below a bridge supporting the checker and around the checker to flues. It required approximately twelve hours to heat this furnace to 1500°C in the combustion chamber. The pressure in this furnace at 1500°C was found to be +0.05 inch water.

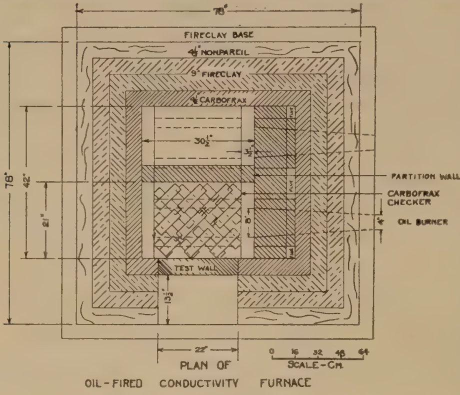

Fig. 1.

The calorimeter (Fig. 4) used was designed after the one described by Dudley. It consisted of a brass casting with a $^1/_{16}$-inch copper plate soldered to the top of the casting and constructed so as to provide for thorough circulation of water.

When the apparatus was connected up for the test, the water entered through the pipe *M*, passed around the center partition *P* to the lower compartment at *K* and returned around *P* to *N*. The rise in temperature of the water passing through the calorimeter was measured by a differential couple. This couple was inserted into rubber stoppers, which were fitted to the $1^1/_2$-inch wells on the inlet and outlet pipes (Fig. 4). These pipes were insulated with $^1/_2$-inch asbestos rope so that the temperature of the water would not change appreciably in passing from the calorimeter to the couple wells.

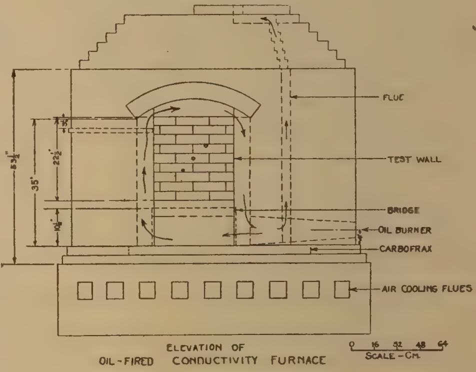

Fig. 2.

The inner and outer guard rings were constructed as shown in Fig. 5. Double circulation of water was obtained in these rings as in the calorimeter. In the inner ring the water entered at *O*, passed through the upper compartment to *S* and returned in the lower compartment to *P*.

The temperature of the outlet water from this ring was held within 0.2°C to that in the calorimeter by means of another differential couple. The calorimeter and inner guard ring were connected to a 60-gallon supply tank in which a constant pressure was maintained.

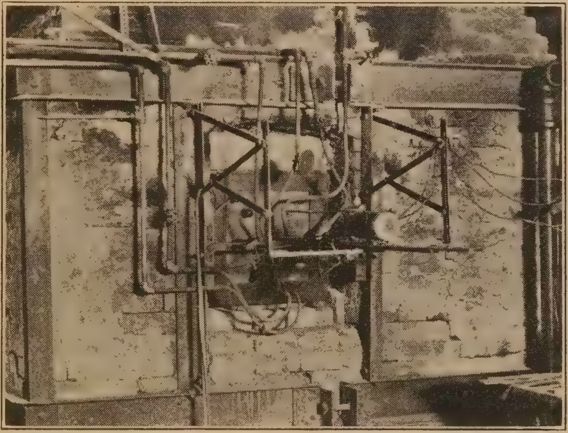

Fig. 3.

The outer guard ring was constructed so that the water entered at *Q*, passed through the compartments as in the inner ring, but in the opposite direction, and out through *R*. The flow of water in this ring was regulated so that the outlet water temperature was within 5°C of that of the calorimeter. The temperatures of the outlet water of the calorimeter and outer ring were determined by means of thermometers inserted in the water pipes near the apparatus. The outer ring was connected directly to the main water line.

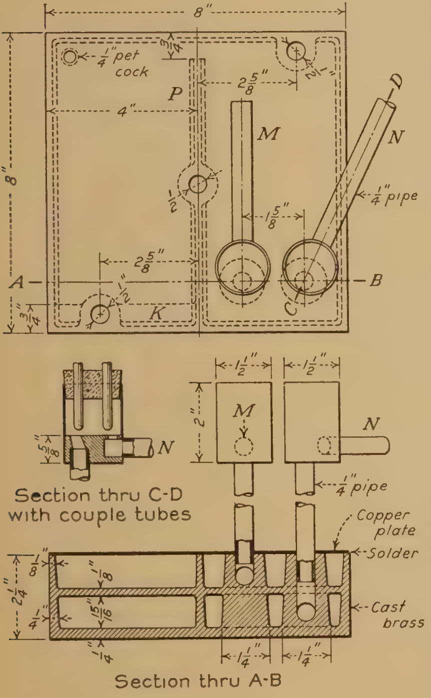

Fig. 4.—Calorimeter.

The apparatus was connected to the water lines with $^3/_8$-inch thin-wall rubber tubing. On the outlet water tubes of the calorimeter and rings screw clamps were placed for close regulation of the flow of water. It was found that if these clamps were put on the inlet tubes the apparatus would not be filled completely with water. This was due to the siphon effect of the drain pipes. The pet cocks were necessary on the calorimeter and rings to release the air while filling the apparatus with water. The pet cocks on the rings were kept open slightly during the tests so that air pockets were prevented. Drain tubes from these pet cocks were provided. There were no air pockets formed in the calorimeter after it was once filled with water.

Operation of Calorimeter

In using the calorimeter with the rings described there could be heat supplied to the calorimeter only through the two faces (1) from the test wall and (2) from the warm air surrounding the apparatus. In order to decrease the heat supplied by the air a $^1/_8$-inch asbestos cover plate was fitted over the top face of the calorimeter and inner guard ring. There was no insulation placed over the outer ring. Asbestos twine was packed between the inner and outer rings and around thermocouple tubes to prevent convection currents as much as possible. Asbestos rope was used for packing between the test wall and the outer guard ring.

In order to determine the amount of heat transmitted to the calorimeter from the test wall, it was first necessary to determine the exact amount of heat which would be transferred through the cover plate for various temperature differences.

To do this the calorimeter was fitted up with differential couples and water connections just as for a regular run. Instead of mounting the calorimeter on the furnace wall, it was suspended in a large wooden box enclosed on all six sides, and an asbestos board (same as on front face) was placed over the back face of the calorimeter. A hot plate and a small electric fan were placed in the bottom of the box. A thermometer was placed one inch from each face which was the position of the thermometer relative to the front face in the later tests.

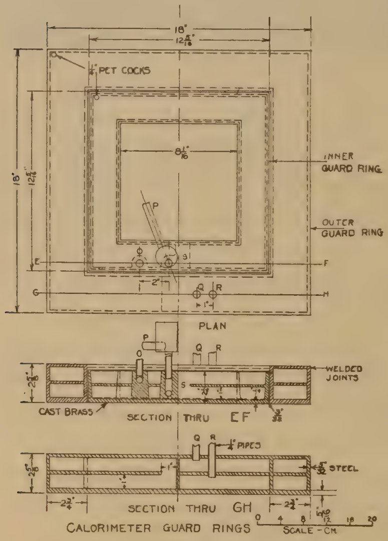

FIG. 5.

The temperature of the box was raised above that of the water entering the calorimeter and maintained at a constant value. The water entering the calorimeter and the guard ring was then adjusted so that the temperature difference at the outlet was less than 0.1°C. The results of the tests and calculations are as follows:

Minimum temp. diff. between air and cal., 13.3°C.
Maximum temp. diff. between air and cal., 30.5°C.
Av. heat flow for 21 tests for 128 in.^{2} × $^1/_8''$ thickness, 0.9600 cals./sec./°C.
Av. heat flow for 21 tests for 1 cm.^{2} × $^1/_8''$ thickness, 0.00116 cals./sec./°C.
Thermal conductivity of asbestos, 0.00037 cals./cm.^{3}/°C/sec.

Measurement of Temperature Gradients The temperature gradients were measured simultaneously at the three points in the wall under the calorimeter by means of three Pt: Pt-Rd thermocouples attached to a slider and supported on the framework (Fig. 3). Three holes $^1/_2$-inch in diameter, drilled to $^1/_4$-inch from the hot surface were fitted with sillimanite pyrometer protection tubes, in which the three thermocouples were inserted to any measured position.

Measurements of temperature gradients in this manner are subject to certain small errors. The protection tubes are of different material from the brick wall; the thermocouple junction is exposed to radiations from the hot end of the hole; convection currents around the tube and the couple may alter the readings.

To determine the magnitude of these possible errors we repeated the tests which Dudley described, going to temperatures as high as 1450°C. Temperature measurements were made in a fire clay wall (1) in open holes (2) open holes with a protection tube liner (3) in a hole closed with clay pieces. The temperature readings in the three cases were identical within the limits of experimental error.

The Thermocouples The differential couples were made of 30 B. & S. gage copper and constantan wire, which was tested and found to be practically homogeneous. The couples were made by mounting the wires on a cardboard and then fusing the ends together in an electric arc. Two separate couples were made in this manner, one composed of 24 junctions for use in measuring the rise in temperature of the calorimeter water, and the other composed of 12 junctions for use in measuring the difference in temperature of the outlet water from the calorimeter and inner guard ring.

The junctions of the couples were wrapped separately with thread and dipped in cellulose acetate solution to prevent short circuiting. The legs of each couple were then sealed in 6 mm. glass tubes with the same solution. The junctions to the lead wires of both of these couples were sealed with casein in test-tubes, which were immersed in oil in order to insure equal temperatures.

These differential couples were calibrated by the use of two "thermos" bottles, three standard thermometers and the precision potentiometer. One leg of the couple to be calibrated was inserted in a stopper with one standard thermometer so that the immersion mark on the thermometer was at the top of the water in the bottle. The other leg of the couple was arranged in the second bottle with another standard thermometer.

The water in one bottle was brought to 17–18°C and one leg of the couple and thermometer inserted. This leg of the couple was marked so that it would be placed in the colder water in the future tests. Care was always taken to have the couple and thermometer at the same depth. The other leg of the couple and Fahrenheit thermometer were inserted in the other bottle containing water at a little higher temperature than that in the first bottle. After the temperature of the water in both bottles became practically constant the potentiometer and thermometers were read as nearly simultaneously as possible. The water in the second bottle was warmed slightly and the same procedure followed. This process was continued until the limit of the Fahrenheit thermometer scale was reached. With greater temperature differences the −18°C to 110°C thermometer was used in the warm water. The same procedure was continued until a temperature difference of 40°C was obtained. The calibration curves for the large couple were plotted on a large scale so that temperatures could be read directly to 0.05°C. The e. m. f. generated by the large couple was practically twice that of the small couple for the same temperature difference. A galvanometer deflection of 1 cm. with the small couple was equivalent to an average of 0.02°C temperature difference. For 0°C difference in temperature the deflection was practically nil.[1]

Method of Conducting Tests

The Walls The thermal conductivity tests were made on the following walls:

1. 9 -inch carborundum No. 1A
2. $4^1/_2$-inch carborundum No. 1B
3. $4^1/_2$-inch carborundum No. 1C
4. $4^1/_2$-inch carborundum No. 2
5. $4^1/_2$-inch carborundum No. 3
6. $4^1/_2$-inch carborundum No. 4
7. $4^1/_2$-inch carborundum No. 5
8. 9 -inch carborundum No. 1A and $4^1/_2$-inch fire clay No. 26
9. 9 -inch carborundum No. 1A and $4^1/_2$-inch fire clay No. 75
10. $4^1/_2$-inch carborundum No. 1C and $4^1/_2$-inch fire clay No. 26
11. $4^1/_2$-inch carborundum No. 2 and $4^1/_2$-inch fire clay No. 26
12. $4^1/_2$-inch carborundum No. 2 and $4^1/_2$-inch fire clay No. 75
13. $4^1/_2$-inch carborundum No. 3 and $4^1/_2$-inch fire clay No. 26
14. $4^1/_2$-inch carborundum No. 4 and $4^1/_2$-inch fire clay No. 26
15. $4^1/_2$-inch carborundum No. 5 and $4^1/_2$-inch fire clay No. 26

The brick used were all standard $2^1/_2$ x $4^1/_2$ x 9-inch.

Before making up the test walls the brick were arranged in the position in which they were later to be placed in the wall. It was necessary to grind down the edges of several of the brick so that they would fit together closely. The brick were then placed approximately $^1/_{32}$ inch apart to allow for the layer of cement, and, by the use of a templet, the positions of the three holes for measuring the temperature gradient were marked.

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[1] This electrical measuring equipment was designed and installed by W. G. Soley, of this laboratory, whose valuable assistance is hereby acknowledged.

In the 9-inch walls the brick were placed so that the temperature gradient was through the 9-inch dimension. In the $4^1/_2$-inch walls they were placed so that the gradient was through the $4^1/_2$-inch dimension.

In the tests on composite walls the carborundum walls were insulated with fire clay brick. These brick were arranged so that the gradient was through the $4^1/_2$-inch dimension. The temperature gradient holes through the insulating walls were made to coincide with those in the carborundum wall. The joints of the two walls were made to mis-match as much as possible.

The carborundum test brick were all laid up with a fine plastic carborundum cement of similar composition to that of the brick. A plastic fire clay cement was used in laying up the fire clay brick. After the wall was completed the surface under the calorimeter and guard rings was covered with a thin layer of the same cement which was later smoothed off and made perfectly flat with a steel straight-edge.

After completing the conductivity test on the single wall, the insulating wall was laid up in the same manner. A thin layer of fire clay cement was also placed between the walls to insure perfect contact.

Set-Up of Calorimeter After drying the test wall, the calorimeter and guard rings were placed against it so that the temperature gradient holes in the brick coincided with those in the calorimeter. The apparatus was then held firmly against the wall by means of clamp screws that were fitted to the framework shown in Fig. 3.

Heating of Furnace After the calorimeter and guard rings were adjusted the apparatus was connected to the water lines. The furnace was heated for approximately 12 hours to obtain 1500°C in the combustion chamber. The oil supply to the burner was then regulated so that the temperature of 1500°C ±15°C would be maintained throughout the test. The air supply to the burner was kept constant. In the meantime, the clamp on the outlet tube from the calorimeter was regulated so that the flow of water was not over three kilograms per minute. The clamp of the outlet tube of the inner guard ring was also regulated so that the temperatures of the water from the calorimeter and guard ring were approximately the same. The flow of water through the outer guard ring was hand regulated throughout the test so that the temperature was within 5°C of that of the calorimeter.

After the furnace had been kept at equilibrium for approximately $^1/_2$ hour, the rise in temperature of the calorimeter water was determined by the potentiometer and the difference in temperature of the calorimeter and guard ring outlet water also determined. Close adjustments were then made on the outlet tube of the inner guard ring until the temperature difference in the outlet water of the two compartments was within 0.2°C, *i. e.*, 10 cm. deflection as indicated by the galvanometer. If the change in potentiometer reading was not over 1 cm. or 0.1°C in $^1/_2$ hour, the furnace and apparatus was considered to be in equilibrium and ready for the test. It usually required two to two and one-half (2 to $2^1/_2$) hours to secure equilibrium after the furnace was heated to 1500°C.

The Set-Up of Thermocouples

The three thermocouples for measuring the temperature gradient were fitted with $^1/_8$-inch 2-hole insulators and inserted in the protection tubes and pushed back as far as possible into the holes in the wall. The insulators were then clamped to the slider and the elements were bent so as to prevent any movement through the insulators. The cold junctions of the couples were inserted into glass tubes in a "thermos" bottle filled with ice.

With the couples arranged in this manner, they were connected to a potentiometer and the temperature readings taken simultaneously in three points in the wall.

After the apparatus was in equilibrium and the couples arranged as described above, the actual test was started. The first temperature gradient readings were taken with the couples in the wall at full depth. The slider was then pulled out 0.4 inch and readings taken. This was repeated until the slider reading was 4 inches, after which the couple was moved to its original position and the readings taken. During this time the water passing through the calorimeter was collected and weighed. After balancing the dry cells of the potentiometer against the standard cell, the slidewire readings were taken for zero deflection of the galvanometer. The temperature difference between the outlet water of the calorimeter and inner guard ring was also read. If the deflection was greater than 10 cm. or 0.2°C adjustments were made on the clamp on the outlet tube of the guard ring to equalize the temperatures. Temperature readings were taken every five minutes for one hour. The total weight of water flowing through the calorimeter during that time was then obtained.

With the thermocouples in their original position the same process was repeated as a check test. Thus for $4^1/_2$-inch walls two one-hour tests were made with the furnace at practically a constant temperature. For the composite walls each test required $1^1/_2$ hours. The temperature gradient readings were taken every 0.5 inch instead of every 0.4 inch as in the $4^1/_2$ inch-walls.

After completing the tests on a wall, the couples were marked at the end of the protection tubes when they were at full depth. The protection tube was also marked at the face of the calorimeter. The couples and tubes were then removed and measurements taken to determine accurately the depth of the hot junction of each couple in the wall at the initial position.

Calculation of Thermal Conductivity

With the temperature of the inner guard ring equal to that of the calorimeter the total heat flow Q_T from both faces of the calorimeter was equal to the sum of the heat flow from the test wall Q_W and that from the air Q_A through the opposite face. The value of Q_T was found by the formula:

$$Q_T = \frac{W \times t}{T \times A}$$

where W = wt. of water in grams
t = °C rise in temp. of water
T = time in seconds
A = area of the calorimeter in sq. cm.

Therefore, Q_T is in gm. calories /cm.²/sec.

Q_A was determined by the formula:

$$Q_A = K_1(t_1 - t_2)$$

where K_1 = ther. condy. of $^1/_8''$ asbestos cover in gm. cals./cm.²/°C/sec.
t_1 = temp. in °C of air 1 inch in front of calorimeter
t_2 = av. temp. in °C of calorimeter
$= t_3 - \frac{t}{2}$ where t_3 is the temp. of the outlet water of the calorimeter.

Therefore, $Q_T - Q_A = Q_W$ in gm. cal./cm.²/sec.

The data and calculations of $4^1/_2''$ of carborundum No. 4, Run No. 29, Test No. 55, are as follows:

Net wt. of water..	129,630 gms.
Av. temp. of calorimeter outlet water..................	30.2°C
Av. temp. of air 1″ in front of calorimeter..............	56.2°C
Av. rise in temp. of cal. water.........................	14.97°C
Av. temp. of cal. $= 30.2 - \frac{14.97}{2}$	22.7°C
Area of calorimeter (effective).........................	64 sq. in.
Time of test..	60 min.
Conductivity of asbestos cover ($^1/_8''$ thick).............	0.00116 cal./cm.²/°C/sec.

$$Q_T = \frac{129{,}630 \times 14.97}{60 \times 60 \times 64 \times 2.54^2} = 1.306 \text{ cals./cm.}^2\text{/sec.}$$

$Q_A = 0.00116\ (56.2 - 22.7) = .039$ cals./cm.²/sec.
$Q_W = Q_T - Q_A = 1.267$ cals./cm.²/sec.
Q_W (Test No. 56) = 1.270 cals./cm.²/sec.
Av. = Q_W (2 tests) = 1.269 cals./cm.²/sec.

Since the temperature gradients and the heat flow for the two tests did not usually vary over 2–3%, the averages were taken for the determination of the thermal conductivity. When there was a greater variation than this the run was repeated. The average temperature gradient curves for the single and composite walls are shown in Figs. 6, 7 and 8. These curves are extrapolated through the last $^1/_4$ inch to the fire side of the

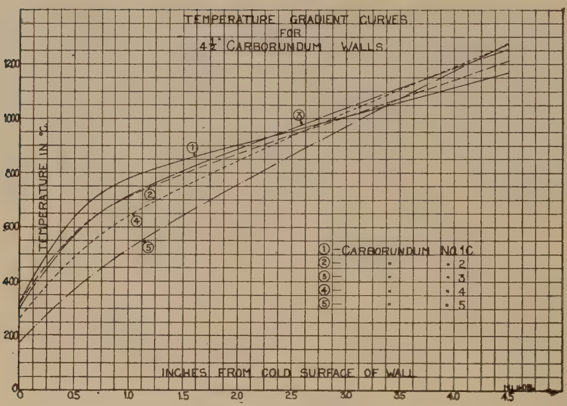

Fig. 6.

wall. They were originally plotted so that temperatures could be read directly to 2°C and distances to 0.01 inch. By the use of these curves the gradient or temperature drop per unit distance could be determined very accurately at any temperature and the conductivity, K, calculated as follows:

$$K = \frac{Q_W \times L \times 2.54}{(t_1 - t_2)}$$

where L = distance in wall in inches; $t_1 - t_2$ = temp. drop in °C. Therefore, K is in gm. cals./cm.^{3}/°C/sec.

Run No. 29, Average of Tests No. 55 and 56

Temperature, °C	Av. temp., °C	Temperature gradient (Av. of 6 curves) Temp. diff., °C	Distance, in.	Thermal conductivity K in gm. cal./cm.^{3}/°C/sec.
780– 822	801	42	0.22	0.0169
880– 920	900	40	.22	.0177
986–1014	1000	28	.16	.0184
1080–1118	1099	38	.22	.0187
1176–1220	1198	44	.27	.0198

$$K_{801} = 1.269 \times 2.54 \times \frac{0.22}{42} = 0.0169 \text{ gm. cal./cm.}^3/^\circ\text{C/sec.}$$

This graphical method of determining the temperature gradient was found to be less involved and more accurate than the one used by Dudley. He assumed that the temperature gradient curve was a section of a parabola and calculated the equation of the curve from three known points. The thermal

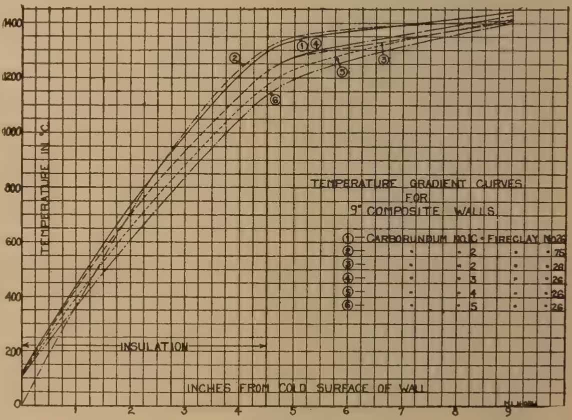

Fig. 7.

conductivity at different temperatures was then determined by taking the first derivative of the equation. Obviously starting with the assumption that the temperature gradient curve was a parabolic section, the thermal conductivity-temperature curves were necessarily straight lines since the first derivative of a second degree equation is a linear function.

In our work it was found that the thermal conductivity-temperature curves were not all linear functions. It was also found that it was practically impossible to calculate an equation for the gradient curve that would fit the actual data accurately. For these reasons the above described graphical method was used for calculating thermal conductivities.

Brick Used for Thermal Conductivity Test The Nos. 1A, 1B, 1C brick were made of carborundum recrystallized in an electric furnace. The other carborundum brick contained ceramic bonds and were kiln fired at approximately 1350°C. The brick No. 26 were coarse, fairly open, first quality fire clay. Brick No. 75 were extremely porous fire clay products also fired at about 1350°C.

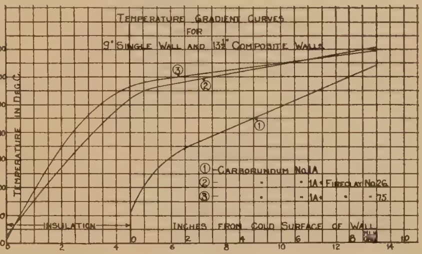

Fig. 8.

In selecting the brick for test the apparent densities of several were first determined, and only those whose apparent densities were near the average of the lot were used in the test wall. In the wall directly under the calorimeter the brick with no greater variation in apparent density than 0.04 gms./cc. were used.

After the completion of the tests on each wall the brick under the

Table I

	Carbo No. 1A	Carbo No. 1B	Carbo No. 1C	Carbo No. 2	Carbo No. 3	Carbo No. 4	Carbo No. 5	Fire clay No. 26	Fire clay No. 75
Apparent density (grams per cc.)	2.05	2.07	2.20	2.48	2.35	2.36	2.31	2.05	0.67
Porosity[1]	34.1	33.8	29.5	18.4	20.7	17.7	18.9	26.8	74.2
Ignition	0.17	0.00	0.00	0.88	0.24	0.02	0.10	0.31	0.00
SiO_2	8.02	4.50	4.50	14.72	23.31	36.80	38.76	58.50	56.90
SiC	91.51	93.20	93.20	80.10	68.50	52.60	48.35		
Al_2O_3	0.20	1.33	1.33	1.47	5.58	8.10	11.63	34.48	37.70
Fe_2O_3	0.65	1.03	1.03	1.33	1.57	1.97	1.97	3.52	2.37
TiO_2								1.80	1.74
CaO								0.29	0.82
MgO								0.62	0.20
Total	100.55	100.06	100.06	98.50	99.20	99.49	100.81	99.52	99.73

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[1] Calculated assuming sp. gr. SiC = 3.17; sp. gr. fire clay = 2.60.

calorimeter were sampled for chemical analysis. The samples were taken from the central, vertical section of the test wall.

The average apparent densities and chemical analyses of the brick are shown in Table I.

Results

Thermal Conductivity In the preliminary work a 9-inch carborundum wall was used and checks made on two separate runs (Nos. 3 and 5). Tests were then made on the same wall backed with various kinds of insulation after which another run (No. 10) was made on the 9-inch wall to check the original results, and to determine if there was any change in the conductivity due to changes in the refractories. The results of the three runs on the 9-inch wall are given in Table II.

TABLE II

Run no.	Temperature, °C	Heat flow Gm. cal./cm.^{2}/sec.	Thermal conductivity Gm. cal./cm.^{3}/°C./sec.	
3*a*	640–1295	1.525	0.0416	
3*b*	665–1340	1.582	.0417	
5*a*	685–1320	1.392	.0390	
5*b*	678–1330	1.498	.0408	
Average		1.499	.0408	±0.0004
10*a*	672–1205	1.305	.0404	
10*b*	710–1283	1.358	.0391	
Average		1.332	.0398	± .0005
Average of 3 runs		1.415	.0403	± .0004

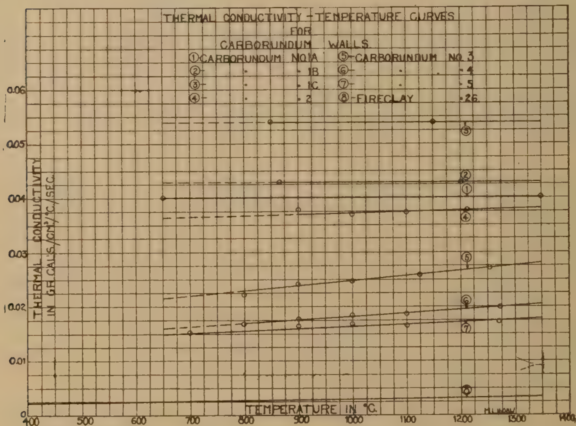

FIG. 9.

These tests show that the results on a given wall can be relied upon to within approximately 1%.

The results on single and composite walls are shown in Table III. The curves showing the change in thermal conductivity with temperature are shown in Figs. 9, 10 and 11. It will be noted in Fig. 9 that the thermal conductivity for carborundum brick does not change rapidly with temperature. With the practically pure carborundum refractory the thermal conductivity is constant at temperatures from 650°C to 1350°C.

TABLE III

Carborundum wall	Insulation	Per cent SiC	Av. heat flow		Temp. gradient at 1350°C (2462°F)		Ther. condy. of Carbo wall at 1350°C (2462°F)	
			Gm. cal/cm.^{2}/sec.	B.t.u./ft.^{2}/hr.	°C/cm.	°F/in.	Gm. cal./cm.^{3}/°C/sec.	B.t.u./ft.^{2}/in./°F/hr.
9″ Carbo No. 1A	None	91.51	1.415	18,780	35.2	160.7	0.0403	116.9
9″ Carbo No. 1A	4½″ Fire clay No. 26	91.51	0.215	2,850	14.0	64.1	0.0153	44.4
9″ Carbo No. 1A	4½″ Fire clay No. 75	91.51	0.075	990	10.1	46.2	0.0074	21.5
4½″ Carbo No. 1B	None	93.20	1.801	23,900	41.9	191.7	0.0430	124.8
4½″ Carbo No. 1C	None	93.20	2.314	30,710	42.7	195.1	0.0542	157.3
4½″ Carbo No. 1C	4½″ Fire clay No. 26	93.20	0.293	3,890	9.4	42.7	0.0314	91.1
4½″ Carbo No. 2	None	80.10	2.170	28,800	56.8	260.0	0.0382	110.9
4½″ Carbo No. 2	4½″ Fire clay No. 26	80.10	0.241	3,200	12.0	54.8	0.0201	58.3
4½″ Carbo No. 2	4½″ Fire clay No. 75	80.10	0.074	980	5.8	26.5	0.0127	36.9
4½″ Carbo No. 3	None	68.50	1.476	19,590	52.5	240.0	0.0281	81.5
4½″ Carbo No. 3	4½″ Fire clay No. 26	68.50	0.254	3,370	13.8	63.1	0.0184	53.4
4½″ Carbo No. 4	None	52.60	1.269	16,840	62.2	284.5	0.0204	59.2
4½″ Carbo No. 4	4½″ Fire clay No. 26	52.60	0.289	3,840	15.4	70.4	0.0187	54.3
4½″ Carbo No. 5	None	48.35	1.369	18,170	77.0	352.0	0.0178	51.7
4½″ Carbo No. 5	4½″ Fire clay No. 26	48.35	0.302	4,010	17.0	78.3	0.0176	51.1

Effect of Gas Diffusion

We believe that the high values for the carborundum brick No. 1C are due to gas diffusion outward toward the calorimeter.

The surface of this wall on the fire side was not coated with cement as in the case with the other walls. Attention has been called by Howe and Phelps[1] to the abnormal effects on thermal conductivities due to penetration of hot gases through the refractories.

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[1] Howe and Phelps, *Jour. Amer. Ceram. Soc.*, **5**, 420 (1922).

Effect of Porosity of Refractory

In order to determine the relation between the thermal conductivity at a given temperature and the percentage of silicon carbide in the carborundum brick, it was necessary to consider the effect of the porosity of the brick. In the case of the fire clay brick with 26% and 74% porosities it was found that the thermal conductivity at 1350°C was approximately inversely proportional to the porosity. With the assumption that the same relation would hold for carborundum brick the thermal conductivities at 1350°C for the uninsulated walls were calculated for zero porosity, and finally for 15, 20, 25, 30 and 35% porosity as shown in Table IV. Figure 12 shows the change in conductivity with increased percentages of carborundum for these porosities.

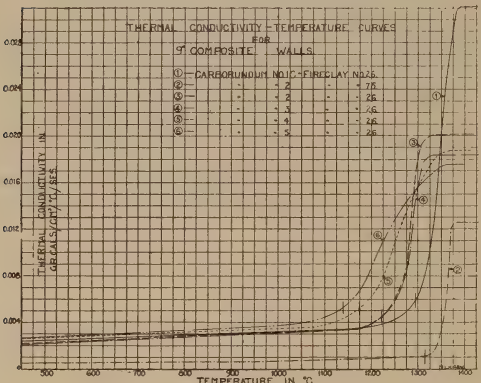

FIG. 10.

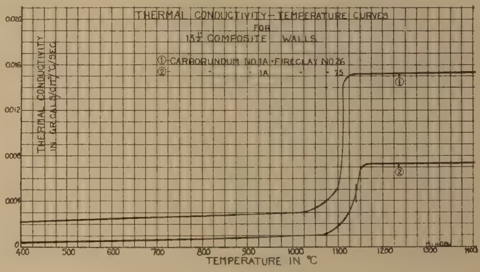

FIG. 11.

Conductivity Related to Heat Flow

Figures 10 and 11 show the very rapid rise in thermal conductivity in the carborundum portion of the composite walls. In comparing the thermal conductivities of the single and insulated carborundum walls, in Table III, it is noted that there is a marked decrease in the conductivity at a given temperature when the carborundum is insulated. This indicates that the

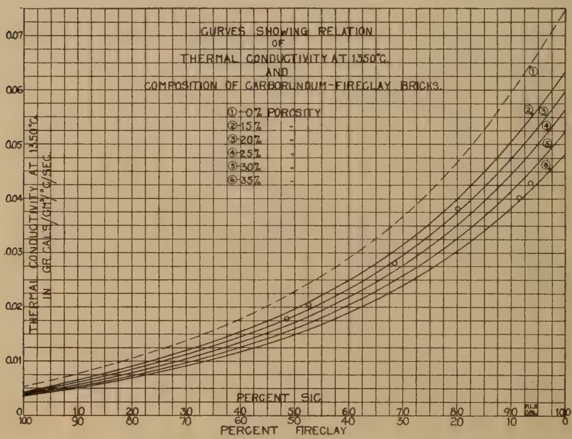

FIG. 12.

TABLE IV

THERMAL CONDUCTIVITY AT 1350°C

Single wall	Per cent SiC	Per cent porosity	Experimental value	Calc. for 0% porosity	Calc. for 15% porosity	Calc. for 20% porosity	Calc. for 25% porosity	Calc. for 30% porosity	Calc. for 35% porosity
Carbo No. 1A	91.51	34.1	0.0403	0.0649	0.0552	0.0519	0.0487	0.0454	0.0422
Carbo No. 1B	93.20	33.8	0.0430	0.0611	0.0519	0.0489	0.0458	0.0428	0.0397
Carbo No. 2	80.10	18.4	0.0382	0.0468	0.0398	0.0374	0.0351	0.0328	0.0304
Carbo No. 3	68.10	20.7	0.0281	0.0354	0.0301	0.0284	0.0266	0.0248	0.0230
Carbo No. 4	52.60	17.7	0.0204	0.0248	0.0211	0.0198	0.0186	0.0174	0.0161
Carbo No. 5	48.35	18.9	0.0178	0.0219	0.0187	0.0176	0.0165	0.0154	0.0143
Fire clay No. 26	0	26.8	0.0038	0.0052	0.0044	0.0041	0.0039	0.0036	0.0034

conductivity is related to the heat flow or temperature gradient. Figure 13 shows the relationship between the thermal conductivity at 1350°C and the heat flow. It will be noted from these curves that in the case of single walls where the temperature gradient is large, the change in conductivity with heat flow is small compared to that in case of composite walls. The conclusion to be drawn from this is that thermal conductivity data for carborundum obtained with large temperature gradients is only applicable in furnace walls where similar conditions are present. With highly insulated walls the effect of the temperature gradient on the thermal conductivity should be taken in consideration. This added variable in the calculation of heat balances will, of course, complicate furnace problems, but it is of such a magnitude in the case of carborundum that it cannot be neglected.

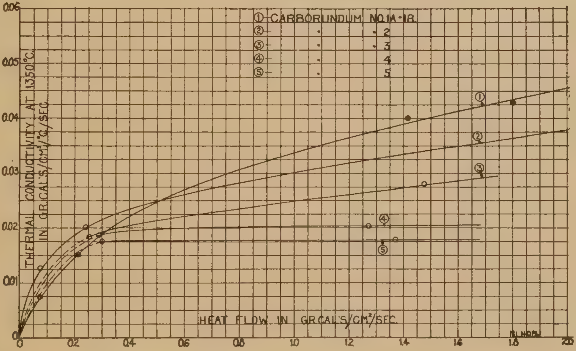

FIG. 13.—Thermal conductivity-heat flow curves for carborundum brick.

Surface and Joint Resistance

In using thermal conductivity data in these problems the question of surface and joint resistances to heat flow in the walls has often been raised. It is expected that the joint resistances of various walls would be approximately the same, but gas-film resistances at the inside surfaces would be quite variable in different installations depending chiefly upon the velocity of the gases in the furnaces. In our experimental work the velocity of the gases was kept approximately constant, but the temperature at the hot surface was measured in only one wall. The temperature of the gases in the combustion chamber is not the same as that at the surface of the brick unless the heat flow through all the furnace walls is uniform. In the tests on the single walls the heat flow through the test wall was several times greater than that through the furnace walls so the temperature at the surface of the test wall was considerably lower than that of the furnace gases. The average difference between the temperature at the surface from the curves, Fig. 6, and that of the gases was found to be 260°C.

In the case of the composite walls the heat flow through the test wall was approximately the same as that through the furnace walls so that the average difference between the temperatures at the surface from the curves in Fig. 7 and that of the gases was approximately 80°C. To confirm this calculation a test was carried out on a $4^1/_2$- inch fire clay wall and the temperature drop at the hot surface of the brick was measured. This was done by drilling a $^1/_8$-inch hole through the last $^1/_4$-inch of the brick in the center temperature gradient hole and inserting a Pt: Pt-Rd thermocouple with $^1/_8$- inch insulators into the hole until the junction was even with the surface of the brick. The temperature gradient curve obtained as in a regular test was then extrapolated to the hot surface brick and the difference in the two surface temperatures thus obtained was the measure of the surface resistance. The temperature drop at the fire clay surface was found by this method to be 95°C.

The joint resistance between the carborundum and the insulation in the 9- inch composite walls was determined by extrapolating the temperature gradient curves in each wall to the joint. The average drop due to this joint resistance was found to be approximately 30°C. This agrees with the results obtained by F. T. Snyder[1] regarding the comparatively low temperature drop at the joints at high temperatures. In calculating the resistances to heat flow through composite walls the assumption may therefore be made that the temperature drop at the hot surface is approximately 80°C, and that at each joint is 30°C.

Application of Results

Single Walls In the refractories through which the maximum heat transmission is desired comparatively thin single walls are used if they have sufficient strength to withstand the necessary loads. For comparison in such cases calculations (Table V) have been made

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[1] Snyder, *Jour. Amer. Electrochem. Soc.*, **18**, 235 (1910).

TABLE V

Furnace temp., °F	Outside temp., °F	Surface drop, °F	Brick temp. drop, °F	Total temp. drop, °F	K_1 carbo B.t.u./ft.²/in./°F/hr.	K_2 fire clay B.t.u./ft.²/in./°F/hr.	Heat flow B.t.u./ft.²/hr.
				4½″ Carbofrax			
2732	1112	144	1476	1620	108.5		35,600
2372	968	144	1260	1404	107.4		30,100
2012	824	144	1044	1188	106.2		24,700
1652	680	144	828	972	105.0		19,340
				4½″ Refrax			
2732	1256	144	1332	1476	117.0		34,600
2372	1094	144	1134	1278	117.0		29,500
2012	932	144	936	1080	117.0		24,350
1652	770	144	738	882	117.0		19,200
				4½″ Fire clay			
2732	446	144	2142	2286		8.42	4,010
2372	392	144	1836	2980		7.84	3,200
2012	338	144	1530	1674		7.26	2,470
1652	284	144	1224	1368		6.68	1,820

on the amount of heat energy transmitted through carbofrax, refrax, and fire clay walls for temperatures of 2732°F, 2372°F, 2012°F, and 1652°F (1500°C, 1300°C, 1100°C, and 900°C), in the combustion chamber. The thermal conductivities used in these calculations were the mean values obtained from actual tests over the temperature ranges shown in Figs. 14, 15 and 16. On these gradient charts the temperatures of the outside surface are approximate with the temperature of the surrounding air about 20°C, and the brick are exposed to no appreciable amount of wind. In all

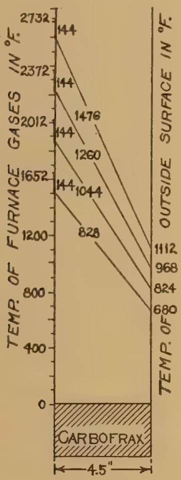

FIG. 14.

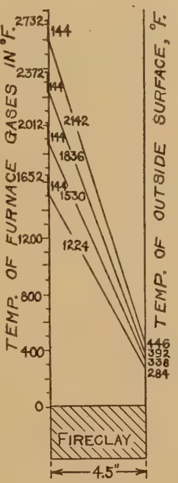

FIG. 15.

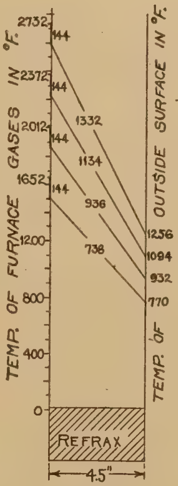

FIG. 16.

these gradients the temperature drop due to the gas film on the hot surface of the brick is assumed to be 144°F (80°C). It is, of course, understood that this value is subject to variation with different velocities of the gases in the combustion chamber. The furnace used for test was, however, operated under conditions very similar to those in commercial furnaces so 80°C represents the magnitude of the surface drop in these furnaces.

The heat flow curves (Fig. 17) show the amount of heat energy transmitted in B.t.u./sq. ft./hr. through walls with various temperature drops which include in each case the surface drop of 80°C. Thus, it is only necessary to measure the temperature of the gases and that of the outside surface and the heat loss per unit area for this temperature drop is at once found. In cases where calculations are to be made for electric furnaces the same curves can be used if the temperature of the hot surface is measured. This temperature is then 80°C lower than that of the furnace gases.

Comparison of Fire Clay and of Silicon Carbide

From these curves (Fig. 17) the enormous amount of heat transmitted through carborundum as compared to that transmitted through fire clay is shown. With a temperature drop of 1450°F there is seventeen times the amount of heat energy conducted through the refrax as through fire clay of the same thickness. In actual practice there is seldom the same drop in the two cases, but even with the temperature drop shown in Figs. 14, 15 and 16 there is approximately nine times the heat conducted through the carborundum as through fire clay. The values (Fig. 17) for carbofrax are slightly lower than those for refrax.

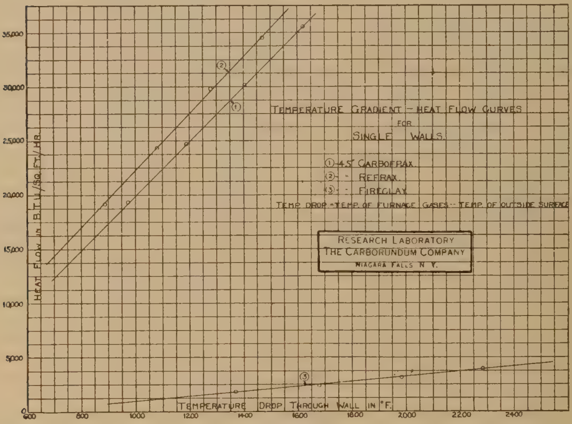

Fig. 17.

In a radiation furnace where the heat is removed quickly from the refractory surface (there being a large temperature gradient) it is at once seen from these curves how much the efficiency of the furnace would be reduced by the use of fire clay or similar refractory material. In small muffles, coke ovens, Dressler kilns, "Carbo Radiant" furnaces, etc., in which the quantity of heat transmitted through a wall is very large, the high thermal efficiency of carborundum is at once recognized.

From the charts (Figs. 14, 15, and 16) the surface temperature of carborundum as compared to fire clay will also be noted. This high temperature together with the high emissivity, which has been found to be nearly double that of fire clay, makes carborundum refractories excellent radiators of heat.

Relative Time Required to Heat Refractories

In applications in which the heat transmission is not so important as the diffusivity, it is desirable to know the relative time required to heat the refractories to a given temperature. In the calculations on carbofrax, refrax, and fire clay assumptions were made that one surface of the wall was perfectly insulated, that is, no heat lost, and the other surface heated uniformly at 1350°C (2462°F) (the operation temperature of many commercial muffles).

In making these calculations Ingersoll and Zobel's[1] formula was used.

$$T_1 = T_2\left(1 - \frac{4c}{\pi}^{\frac{-h^2\pi^2t}{L^2}} + \frac{4}{3\pi}c^{\frac{-9h^2\pi^2t}{L^2}} \ldots\right)$$

where T_1 = Temperature of insulated surface in °C
T_2 = Temperature of hot surface on °C (constant)
L = Twice the thickness of the wall
k = Thermal conductivity in C. G. S. units
c = Specific heat in C. G. S. units
d = Density
$h^2 = k/cd$

The value of the last term is negligible except when t is very small.

The thickness of the wall was assumed to be three inches. The thermal conductivities, densities, specific heats, etc., used in the calculations are shown in Table VI. It will be noted that the value of the thermal conductivity used for carbofrax and refrax decreases quite considerably with the temperature drop. These values were obtained from curves showing the relationship between temperature drop and thermal conductivity. Different values for time were then substituted in the above formula until a temperature drop corresponding to the conductivity used was obtained. The mean value of the thermal conductivity of fire clay was used over the temperature range from 20°C to 1350°C (2462°F), the conductivity of fire clay being independent of the temperature gradient. The relative heating time for these three refractories is shown in Fig. 18. From these curves it is found that the time required to heat a fire clay wall to within 162°F of the hot surface is 4.9 times that of refrax and 6.3 times that of carbofrax.

In all intermittent furnace operations the time required to heat the furnace walls to a given temperature is an important factor entering in

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[1] Glazebrook's "Dictionary of Applied Physics," page 466.

TABLE VI

Carbofrax

$d = 2.45, c = 0.18, L = 6''$

Time, min.	B.t.u./ft.^{2}/in./°F/hr.	Temp. drop, °F	T_2 °F	T_1 °F
1	111.0	2338	2462	124
3	111.0	1595	2462	867
5	111.0	1026	2462	1436
8	111.0	531	2462	1931
11	92.8(392°F)	401	2462	2051
12	92.8(392°F)	301	2462	2161
18	69.7(257°F)	252	2462	2210
40	42.4(140°F)	104	2462	2358
90	24.7(77°F)	36	2462	2426

Refrax

$d = 2.05, c = 0.16, L = 6''$

1	117.0	2200	2462	262
3	117.0	1210	2462	1252
5	117.0	644	2462	1818
6	117.0	473	2462	1989
11	81.3(392°F)	349	2462	2113
20	50.8(257°F)	238	2462	2224
40	29.0(158°F)	139	2462	2323
100	14.5(95°F)	63	2462	2399

Fire Clay

$d = 2.04, c = 0.19, L = 6''$

10	7.26	2374	2462	88
30	7.26	1876	2462	586
60	7.26	1156	2462	1306
90	7.26	706	2462	1756
120	7.26	430	2462	2032
150	7.26	263	2462	2199
180	7.26	160	2462	2302
210	7.26	97	2462	2365
240	7.26	59	2462	2403

fuel and labor costs. In selecting the best refractory to be used the first cost of the installation may be comparatively high, but this is more than offset by the economies in the operation. Such is the case with carborundum especially in heat treating, enameling muffle furnaces, etc., which perhaps costs ten times as much as fire clay, but commercial reports show 40–50% increase in production and approximately the same percentage decrease in fuel costs without considering the saving of time and labor.

The heat capacity of the charge in most of these furnaces is very low compared to that of the muffle, usually below 5%, so at least 95% of the heat supplied by the gases is absorbed by the refractory walls or lost through the doors and back wall. In the calculations on the heat capacity of furnace walls the assumption was made that there was no loss of heat from one surface and that the other surface was uniformly heated at 1350°C.

Such conditions are approached in most oil and gas fired muffles, since the flue side of the wall is heated quite rapidly to a fairly constant temperature, and the heat loss from the wall on the other side to the charge is very low (2–5%). The loss through the doors and back wall depends upon the furnace construction, but this is usually a small percentage of the total heat supplied. At least, it would be very much the same in the two cases under consideration.

By referring to Fig. 18 then, the relative heating time required in the case of carborundum and fire clay muffles can be emphasized, that is, assuming the same thickness of the walls. Carborundum muffles are usually made with walls 1 to 1.5 inches thinner than fire clay muffles so that the heating time for these muffles is decreased still further in the actual installation.

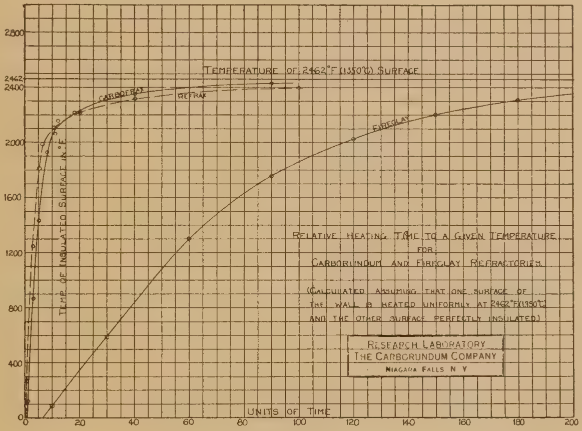

FIG. 18.

In most commercial muffles the temperature drop through the wall is usually below 100°C, while in the fire clay it is 350–400°C so that the flue temperatures must be maintained at 250–300°C higher in order to attain the proper muffle temperature in a reasonable length of time.

Composite Furnace Walls

In a large percentage of furnaces in which carborundum refractories have to be insulated, it is very necessary to select the proper kind and amount of insulation. Many insulating materials do not withstand high temperatures, others withstand the temperatures but transmit too much heat. Nine inches of insulation having a low thermal conductivity may be sufficient in one furnace, while $13^1/_2$ inches or 18 inches may be required in others. The amount of insulation may be limited to the available floor space in a particular plant. With added insulation the increase in the radiation surface may cause excessive heat losses, etc. All these factors make the question of insulation a complicated one.

In order to assist in the solution of some of these problems calculations have been made on six insulated carborundum walls for various temperature drops.

Since it was found in our experimental work that the thermal conductivity (K) of carborundum varied with the amount of heat energy (Q) transmitted, it was first necessary to determine the equation for the relationship between these variables in further calculations in composite walls. The equations were found to be as follows:

$$\text{(1)} \quad \text{For Carbofrax: } K^2 - 0.00557K - 0.00122Q = 0$$

$$\text{(2)} \quad \text{For Refrax: } K^2 + 0.0133K - 0.00204Q = 0$$

(from conductivity data)

In an insulated wall composed of, for example, 4½″ of carbofrax, 4½″ of fire clay and 4½″ of highly insulating material, the relationship between the heat flow and the conductivity of each portion of the wall was expressed by the equation

$$\text{(3)} \qquad Q = \frac{T_1 - T_2}{4.5 \times 2.54\,(1/K - 1/K_2 - 1/K_3)}$$

where $T_1 - T_2$ = Total temperature drop through the wall (excluding the drops at the surface and joints)

K = Mean thermal condy. of carbofrax in C. G. S. units

K_2 = Mean thermal condy. of fire clay in C. G. S. units

K_3 = Mean thermal condy. of insulation in C. G. S. units

In using this equation the temperature drop ($T_1 - T_2$) was assumed and $K_2 - K_3$ determined over the approximate temperature range in each section of the wall. Equations (1) and (3) each having the same two variables were then solved simultaneously and the heat flow through the composite walls calculated. Finally, the temperature drop through each section of the wall was determined by the formula

$$T = \frac{Q \times 4.5 \times 2.54}{K}.$$

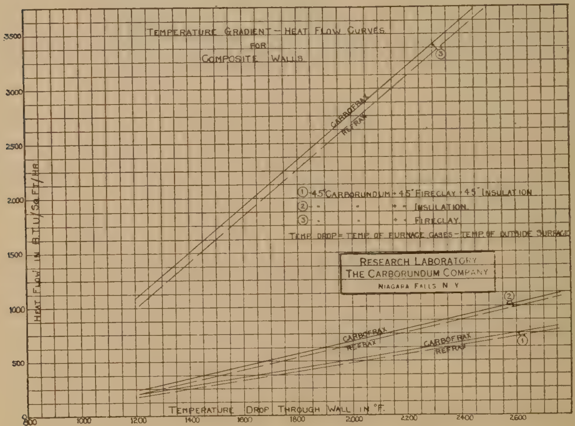

FIG. 19.

Thus, the results were checked if the sum of the temperature drops in each wall was equal to the total assumed drop.

By the use of this method, the heat transmitted through composite walls was calculated for both carbofrax and refrax backed up with fire clay, insulation, and fire clay and insulation combined. The tabulation of the results is shown in Table VII and the heat flow curves for these six walls plotted on Fig. 19. The temperature drop shown on the curves includes the surface drop of 80°C as in the single walls. The joint drop used in the gradient charts (Figs. 20–25 inclusive) was assumed to be 30°C, the average value determined by the actual tests on composite walls.

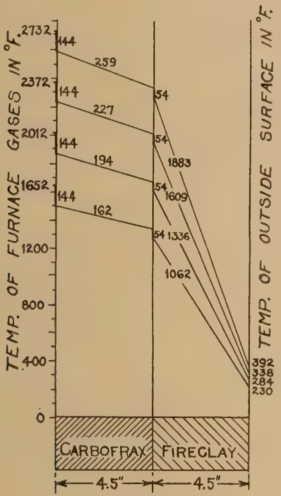

FIG. 20.

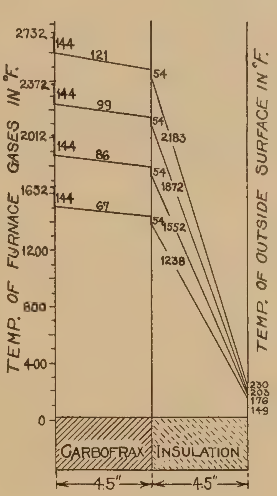

FIG. 21.

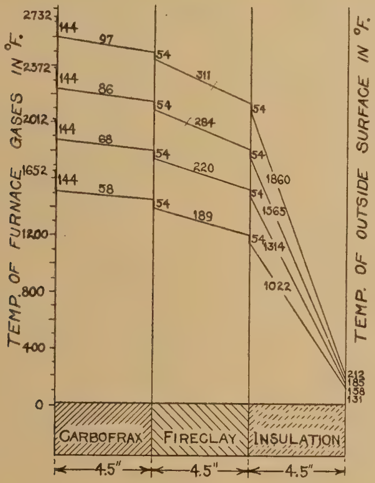

FIG. 22.

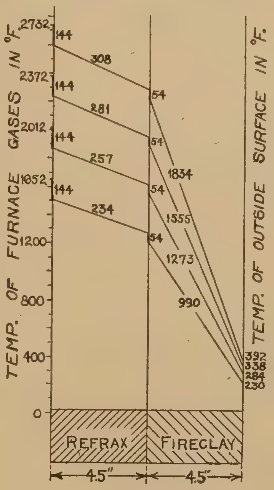

FIG. 23.

In insulating carborundum refractories the materials selected should withstand the maximum operating temperatures. Most insulators will fuse and crack excessively at temperatures above 1050 to 1100°C. As

TABLE VII

Furnace temp., °F	Outside temp., °F	Surface drop, °F	Brick drop, °F	Total drop, °F	K_1 carbo B.t.u./ft.^{2}/in./°F/hour	K_2 fire clay B.t.u./ft.^{2}/in./°F/hour	K_3 insulation B.t.u./ft.^{2}/in./°F/hour	Heat flow B.t.u./ft.^{2}/hour	T_1 carbo, °F	T_2 fire clay, °F	T_3 insulation, °F
$4^1/_2$″ Carbofrax, $4^1/_2$″ Fire Clay, $4^1/_2$″ Insulation											
2732	212	252	2268	2520	32.8	10.44	1.74	716	97	311	1860
2372	185	252	1935	2187	31.0	9.58	1.74	604	86	284	1565
2012	158	252	1602	1854	27.9	8.72	1.45	423	68	220	1314
1652	131	252	1269	1521	25.8	7.88	1.45	329	58	189	1022
$4^1/_2$″ Refrax, $4^1/_2$″ Fire Clay, $4^1/_2$″ Insulation											
2732	212	252	2268	2520	16.3	10.44	1.74	690	191	297	1780
2372	185	252	1935	2187	13.9	9.58	1.74	571	184	268	1483
2012	158	252	1602	1854	10.4	8.72	1.45	395	171	203	1228
1652	131	252	1269	1521	8.4	7.84	1.45	301	162	173	934
$4^1/_2$″ Carbofrax, $4^1/_2$″ Fire Clay											
2732	392	198	2142	2340	60.9	8.42		3520	259	1883	
2372	338	198	1836	2034	55.5	7.84		2800	227	1609	
2012	284	198	1530	1728	49.7	7.36		2150	194	1336	
1652	230	198	1224	1422	44.2	6.68		1580	162	1062	
$4^1/_2$″ Refrax, $4^1/_2$″ Fire Clay											
2732	392	198	2142	2340	50.3	8.42		3440	308	1834	
2372	338	198	1836	2034	43.3	7.84		2710	281	1555	
2012	284	198	1530	1728	36.0	7.26		2060	257	1273	
1652	230	198	1224	1422	28.5	6.68		1470	234	990	
$4^1/_2$″ Carbofrax, $4^1/_2$″ Insulation											
2732	230	198	2304	2502	36.9		2.03	987	121		2183
2372	203	198	1971	2169	33.1		1.74	725	99		1872
2012	176	198	1638	1836	31.1		1.74	602	86		1552
1652	149	198	1305	1503	27.3		1.45	401	67		1238
$4^1/_2$″ Refrax, $4^1/_2$″ Insulation											
2732	230	198	2304	2502	20.9		2.09	950	203		2101
2372	203	198	1971	2169	16.3		1.74	680	191		1780
2012	176	198	1638	1836	13.9		1.74	571	182		1456
1652	149	198	1305	1503	9.9		1.45	366	167		1138

shown in the gradients (Figs. 21 and 24) such materials could not be used unless the operating temperature (furnace gases) was below 1300°C. Where it is necessary to run at higher temperatures the carborundum must be backed up with a higher temperature material, usually common fire clay (Figs. 20 and 23), but the heat losses through this material are excessive. The practice then, is to use both the fire clay and insulation as shown in Figs. 22 and 25.

The principal use of the additional layer of fire clay is to lower the temperature gradient, since it does not reduce the heat losses appreciably as shown in Fig. 19. The difference between curves 1 and 2 (Fig. 19) indicates the small insulating value of this material.

In many furnaces it is necessary to use perhaps 18 inches of common fire clay in order to lower the gradient so that the insulation will withstand the temperatures. All this fire clay material does decrease the heat losses by "straight line" conductivity, but it increases the heat capacity and radiating surface so greatly that this advantage cannot be considered.

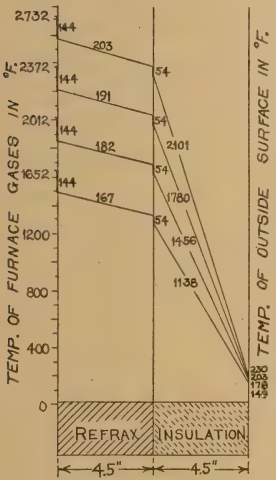

FIG. 24.

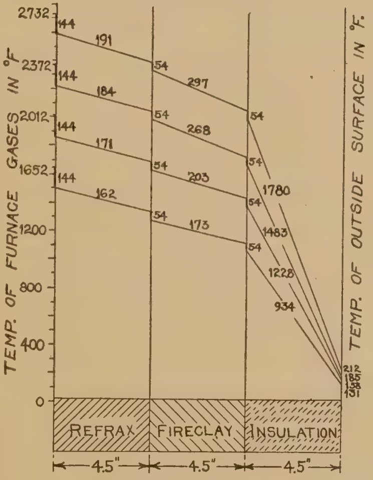

FIG. 25.

Conclusions

In addition to the numerical values for the thermal conductivity of carborundum refractories containing various percentages of silicon carbide and fire clay, we can draw from the data the following conclusions:

1. The thermal conductivity of practically pure carborundum is constant for temperatures ranging from 650° to 1350°C.

2. The thermal conductivity of ceramically bonded carborundum increases with increasing temperature.

3. The thermal conductivity of carborundum refractories decreases with the increase in percentage of fire clay bond.

4. The temperature gradient through a carborundum wall increases with the increase in percentage of fire clay bond in the brick.

5. The thermal conductivity of fire clay is approximately inversely proportional to the porosity.

6. At any given temperature the thermal conductivity of carborundum increases as the amount of heat energy transmitted is increased.

7. At any given temperature the thermal conductivity of the fire clay is practically independent of the amount of heat energy transmitted within the range investigated.

8. The temperature drop due to the gas-film resistance at the hot surface of insulated furnace walls is approximately 80°C under these experimental conditions.

9. The temperature drop due to the joint resistance in composite furnace walls is approximately 30°C under these experimental conditions.

In order to make the experimental data on carborundum refractories of more practical value in the solution of furnace problems, calculations have been made to apply to a number of commercial applications for the determination of:

10. Temperature gradient and heat transmission through single walls as applied to radiation furnaces, coke ovens, "Carbo Radiant" furnaces, tunnel kilns, etc.

11. Thermal diffusivity of single walls for comparison in muffle and other intermittent furnace operations.

12. Temperature gradient in composite walls for use in selecting the insulation that will withstand the operating temperatures.

13. The heat losses in the insulated carborundum walls.

Discussion

C. J. HUDSON:[1] By a perusal of the literature for results of conductivity data, a reader will note the lack of agreement among various investigators. The determination of the true coefficient of conductivity of a material is not an easy thing to make; the apparent result is oftentimes the sum of the true coefficient and other factors creeping in to give an erroneous result. The authors of this paper have taken great pains to eliminate some of these other factors and deserve credit for the careful work which they have done.

The coefficient of conductivity for silicon carbide, as just shown, is considerably higher than any other published result for this material. If the authors had determined the coefficients for a few other materials and had shown them to be in fair agreement with those of other authorities, this high result for silicon carbide would be somewhat more conclusive. The results given for fire clay compare favorably with some of those published by other observers, but the term fire clay is a loose one to use since fire clays differ in properties which in turn may affect their coefficients of conductivity.

A possible explanation for this high result may be in the diffusion of the furnace gases through the refractory wall under test. Howe and

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[1] Norton Co., Worcester, Mass.

Phelps[1] have shown that a slight pressure in a furnace under fire will appreciably raise the temperature within refractory walls some distance from the fire side. The authors have apparently painted the outside of their refractory test walls with a cement, but this would not prevent diffusion of the furnace gases into the holes cut for the thermocouples. The fire side of the test walls seems to have been covered with cement except in one case, but it is doubtful if this covering would prevent the diffusion of gases into the thermocouple holes which were cut to within $^1/_4$ inch of the fire side. This doubtful point could have been partially corrected had the couples been inserted parallel to the plane of the furnace wall instead of perpendicular to it; this change would have also eliminated any radiation and conduction errors in the thermocouple readings.

The thermal conductivity-temperature curves given in Fig. 9 were found to be non-linear functions. This is apparently a mis-statement for all seem to be straight lines and some are constructed by drawing them through only two observation points.

The conclusion that the thermal conductivity of silicon carbide at a given temperature increases with the amount of energy transmitted is interesting. Since this seems to be a property peculiar to silicon carbide and not to fire clay an attempt at an explanation of this phenomenon would have certainly added weight to the conclusion. If the test to prove this had been carried out with the same average temperatures through the piece as was used for the determination of the conductivity coefficients, the result would have been somewhat more conclusive.

Conductivity coefficients of silicon carbide and fused alumina refractories have been published by Norton Company showing a difference of about 15% between them; while these published coefficients appear to be too low, it is thought that the relation still holds. The user of refractories of this type is interested in what conductivity figures will mean to him in terms of fuel expenditure. The authors in this paper state—"of all the refractory materials available commercially, there is none which even approaches silicon carbide or carborundum in its ability to readily transmit heat and at the same time have mechanical strength and chemical inertness to resist the various destructive forces in modern industrial furnaces." There are at least two industrial furnaces in operation where strict comparisons may be made to show that fused alumina refractories do transmit heat as readily as silicon carbide. These two furnaces were at one time equipped with silicon carbide muffles and are now equipped with fused alumina muffles; in neither case has the fuel consumption increased; muffle temperatures are approximately the same for the same temperature in the ware chambers; and in both of these cases the muffles were changed from silicon carbide to fused alumina refractories because the silicon carbide did not possess the necessary chemical inertness.

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[1] Howe and Phelps, *Jour. Amer. Ceram. Soc.*, 5 [7], 420 (1922).

In the transfer of heat through a refractory in a commercial muffle furnace the coefficient of conductivity of the intervening refractory is not the only factor needing consideration, at least film coefficient and emission factor play a part in the drop in temperature between the source of heat and the product to be heated. The emission and film coefficients become of more importance relative to the conductivity coefficient when the refractory is thin. There is nothing in this paper to indicate that in these two factors silicon carbide differs from other refractories. In practical applications they apparently play an important part.

O. B. WESTMONT: The data recorded by Howe and Phelps[1] does indicate the possible effect of the diffusion of gases through the refractory wall upon the thermal conductivity. These data, however, show the changes in wall temperatures for quite a wide variation in pressure (+1.0 to −0.3 inch water). Our conductivity furnace was operated at such a very low pressure (0.05 inch water) that I believe the diffusion of gases would not affect our results appreciably.

Our values for the conductivity coefficient of carborundum and fire clay refractories do not differ greatly from the values recorded for similar refractories by most of the previous investigators.

Our average coefficients for fire clay and highly insulating materials are slightly lower than the average plotted by W. Trinks[2] for the same temperature range. The value for one commercial ceramically bonded carborundum refractory, Curve 5, Fig. 9 (p. 272), is approximately the same as that recorded by Wologdine for the same material. For the purer carborundum refractories the coefficients are, of course, considerably higher.

The statement that "thermal conductivity-temperature curves were not all linear functions" is correct as given. It *is* true that these curves for carborundum are straight lines, but with insulating materials they are not. It will be noted that only the conductivity-temperature curves for the recrystallized silicon carbide materials were drawn through two points. The conductivities for these refractories were practically constant for the temperatures shown (the gradient curves being constant through the major portion of the walls) so it was only necessary to indicate the limiting points in each case.

Our investigations show that the thermal conductivity for carborundum refractories now on the market is approximately four times that of fused alumina for the same temperature range.

F. H. NORTON: I think the authors of this paper should be complimented on the most complete work on thermal conductivity that has ever been done. We must realize that the measurement is one of the most difficult that there is.

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[1] *Loc. cit.*

[2] "Industrial Furnaces," p. 67.

On some conductivity tests that we have made on very dense brick we found the same condition of a falling off of the temperature at the cool face of the brick when using a sliding couple and we were a little suspicious of the result so we finally cemented in the face of the brick a very fine couple which should give the true temperature. In that case we found that the straight line of the higher temperature portion of the brick continued down to the outer temperature reading and the reading on the sliding couple was several hundred degrees low due to the conductivity of the couple wires and I think this is the case in these tests which would make the carborundum lower.

There is another thing that I wanted to bring out in the conductivity talk and that is that the conductivity seems to depend on the amount of heat carried through the walls. This is something that no one has noted before and if substantiated by further tests will prove a very important fact. However, it may be that insufficient guarding of the calorimeter in the thicker walls causes this phenomena. If there is a difference in the temperature between the center and outside of the calorimeter of only a few degrees it will introduce large errors in a wall of the thickness the authors used. We have found it necessary to use a 27-inch guard ring around a calorimeter only four inches in diameter to get a satisfactory guarding with high temperature with fairly good conducting brick.

W. A. KOEHLER: In regard to the thermal conductivity being complicated by diffusion of gases, I think the authors have taken reasonable caution to eliminate the diffusion of gases as completely as possible, although they may not have succeeded in doing so altogether. If we can eliminate diffusion and all other factors affecting the conductivity measurements, we obtain a true conductivity which is a fundamental physical constant. In addition, however, it would also be of value to know what the apparent conductivity would be in actual installations in which the diffusion of gases and all other factors are allowed to take their courses.

R. F. GELLER: What is the definition of conductivity? It seems to me that conductivity is an inherent quality of the material.

CHAIRMAN HARVEY: The pressure differs. In this particular case it is reduced to something like five-hundredths of an inch.

R. F. GELLER: The question has been asked: "What would have been the *conductivity* if the pressure had been greater?"

O. B. WESTMONT: It seems to me that the true thermal conductivity of a refractory is an inherent property of the material under certain conditions just as specific gravity, specific heat, etc. There are, however, so many possible variables entering in the determination of this coefficient that the apparent thermal conductivity may be quite different from the true coefficient. The most practical value then, would be that which is obtained under conditions which more closely approach those in commercial furnaces.

R. F. GELLER: My point is, that the abstract term *conductivity* is being used when "relative conductivity" or perhaps "actual heat conducted" is probably meant. This would, and should necessitate defining the conditions under which the trials were made.

O. B. WESTMONT: I believe we should define all the conditions whenever we determine our conductivity data, but I do not believe we can standardize them. If we secure data under one pressure we have no definite law, such as Boyle's law, for instance, by which we can calculate the coefficient at a different pressure. The same would apply for low temperature conductivity determinations.

In regard to the calorimeter guard ring referred to by Mr. Norton, we found that we had practically linear flow of heat through the test wall under our calorimeter with an 18-inch guard ring. The temperature gradients (Figs. 6, 7, and 8) are the average of the measurements in the three holes in the test wall. The curve for each gradient hole in a given wall did not coincide with the others in many cases due to slightly uneven heating on the fire side. The curves were, however, usually parallel showing that there was practically no lateral flow of heat.

A. S. WATTS[1] AND R. M. KING: Dr. Hartmann and Mr. Westmont emphasize the conclusion that the conductivity of carborundum increases with the quantity of heat actually transmitted. It appears to the writers that two conclusions can be drawn from this data, one being mentioned above and the other that Fourier's law does not hold under the conditions of the experiment.

It is our impression that Fourier's law is based on a condition of kinetic equilibrium within the material being tested. However, if we back up a wall of material of high thermal conductivity with a wall of material of low conductivity we cannot expect the outer wall to take away the heat as fast as the inner wall can deliver it, hence we would expect a damming up of heat at the joint and there would soon be developed a zone where the heat is in static equilibrium or rather what we might call a reservoir where heat is flowing out as fast as it is flowing in. This being the case the conditions of Fourier's law have been changed and hence we feel that we cannot agree with the authors' conclusion. We would rather conclude that Fourier's law does not apply in this particular case.

It is unfortunate that Dr. Hartmann and Mr. Westmont did not obtain more data on carborundum walls of varying thickness. We would like to compare the data obtained on a 9-inch wall of a particular grade with that obtained on a $4^1/_2$-inch wall of the same material, but this is not possible with the data available. However, we note that a 9-inch wall of Carbo No. 1A allows the passage of 1.415 C.G.S. units of heat with the resulting conductivity calculated as .0403 C.G.S. units, and a $4^1/_2$-inch wall of Carbo No. 1B conducts 1.801 units at the rate of .0430 units, and a $4^1/_2$-inch wall of Carbo No. 1C conducts 2.314 units at a rate of .0542 units. Following the conclusion of the paper we could say that this increase in conductivity is due only to the increased heat energy transmitted. This is to be expected if we accept Fourier's law. But we would ask why the increased transmission of heat? We can account for at least a part of this by the higher silicon carbide content in 1B and the increased density in 1C. However, when we note a decrease in heat flow in the composite walls we explain this by saying that the fire clay will not transmit the heat as rapidly as will the carborundum.

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[1] Dept. of Ceramics, O. S. U., Columbus, Ohio.

We would like to call attention to the fact that Carbo No. 4 conducts less heat than does Carbo No. 5 and yet No. 4 has a conductivity of .0204 and No. 5 a conductivity of .0178. Again No. 5 uninsulated conducts four and one-half times as much heat as when insulated but the conductivity is the same in both cases.

If the authors' conclusions are correct regarding carborundum brick, *i. e.*, that increased transmission of heat increases conductivity, why would not any other refractory when backed up with a good insulator show an increase in conductivity with increased quantity of heat transmitted. A fire clay brick backed up with a kieselguhr brick, should display the same properties as the carborundum backed up with fire clay brick. Dr. Hartmann and Mr. Westmont have not presented any data to show that this is not true.

M. L. HARTMANN AND O. B. WESTMONT:[1] Replying to the third paragraph of the discussion by Watts and King, further accurate conductivity data are always desired, and in this case may be forthcoming at a later date. As noted in the paper, the increased heat transmission in the wall 1C is partly explained by the diffusion of gases from the furnace, which experimental defect was corrected in the other experiments.

In comparing the conductivities of two similar walls both the heat flow and temperature gradients of each must be taken into consideration. The thermal conductivity is, obviously, not directly proportional to the heat flow.

With those refractories having a high percentage of fire clay bond, the change in conductivity with heat flow in insulated walls becomes less pronounced. The limit of this change is in the 100% fire clay brick in which the conductivity is apparently independent of the heat flow.

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[1] Written reply to Watts and King discussion.

M. L. HARTMANN AND O. B. WESTMONT:[1] Mr. Hudson's skepticism as to the accuracy of our data because they do not conform to other published information on the thermal conductivity of carborundum refractories seems to us to be hardly justified. Examination of the literature discloses the following:

	Firing temp., °C	Composition	Temp., °C	Thermal condy., C. G. S. units
Wologdine:[2]	1300	87% SiC	300–650	0.019
	1300	87% SiC	230–440	0.027
	1300	75% SiC	420–1000	0.015
Linbarger:[3]	1350	10% Clay Bond	0–1000	0.024
Moores:[4]	..	......	900	0.0235
Beecher (Norton Co.):[5]	..	10% Clay Bond	650–1250	0.00982

Even with the considerable variation in composition and burning conditions, there appears to be fairly good agreement as to the *order of magnitude* of the coefficient, with the exception of the last reference.

We have investigated to some extent the surface film and the emissivity factors of carborundum and fire clay refractories. The surface temperature drop due to the gas film resistance under our test conditions was not appreciably different in carborundum (80°C) from that in the fire clay (95°C). The emissivity of carborundum (page 279) was found to be nearly double that of fire clay.

There appears to be scanty experimental evidence to show so small a difference as 15% between the thermal conductivities of silicon carbide and fused alumina refractories. The results of Watts and King[6] show that the conductivity of "Carbofrax B" is 3.39 times that of "Alundum" at approximately 1000°C. The value recorded by Beecher for "Alundum" is .00833 C.G.S. units for temperatures ranging from 650–1250°C. Our values for two kinds of "carbofrax" refractories for the same temperature range (Curves 4 and 5, Fig. 9) are 2.86 and 4.19 times this value for "Alundum."

The extended use of carborundum refractories for heat transmission in the past few years seems to indicate conclusively the composite opinions of furnace users as to the superior property of carborundum to conduct heat over that of any other refractory material. There are conditions involving chemical activity under which carborundum does not have sufficient life for economical operation, but as a good transmitter of heat, it is not approached by any other refractory material.

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[1] Written reply to C. J. Hudson's discussion.

[2] Wologdine, *Electrochem. and Met. Ind.*, **7**, 383 (1909).

[3] Linbarger, *Chem. and Met. Eng.*, **19**, 489 (1918).

[4] K. T. Moores, Thesis, Mass. Institute of Technology.

[5] Beecher, *Jour. Amer. Ceram. Soc.*, **7** [1], 19 (1924).

[6] Watts and King, *Jour. Amer. Ceram. Soc.*, **6** [10], 1075 (1923).

P. Nicholls:[1] The conclusion arrived at by the authors that the thermal conductivity of a material, or for carborundum at least, varies at a given temperature with the rate of heat flow is so revolutionary that it calls for immediate proof or rebuttal by further tests introducing different test conditions, or eliminating possible sources of error. The fundamental principle of all heat conduction is based on the independence of conductivity and the rate of flow; proof to the contrary would require its entire revision and some new concept of the mechanism of conduction. Moreover, the tests show that the variation is not small but (see Fig. 13) at 1350°C is several hundred per cent.

That the thermal conductivity may and does vary greatly with temperature is of course true, but even then one would expect to find changes in some other physical characteristics of the material if the variation were abnormal, such as from fusing or melting.

The authors suggest that since the material is cellular the conductivity variation with rate of flow may be due to the radiation factor of the transmission across the small air spaces. That such an action would cause the conductivity to vary with the rate of flow is correct, and if the amount were appreciable, the normal heat conduction mathematics could not be applied. The magnitude of this action can be estimated if definite structural conditions are assumed, but the mathematical expressions become rather complicated. However, it is not difficult to show that it is small even for a structure in which all the transfer is by repeated radiations, and none by conduction of the air between the successive layers of material. Imagine a slab made up of very thin parallel laminae with no thermal resistance. If heat flows through this by radiating from one surface to another, it can be shown that the equivalent conductance coefficient, C, between two surfaces, one being at a temperature T degrees absolute temperature, would be of the form $C = a(T^3 \pm T(\Delta T)^2)$, where a is a constant, and ΔT the small difference in temperature between the faces of the two laminae.

It is evident that the value of C would vary rapidly with the temperature T, and since the ΔT would be proportional to the rate of heat flow, C would depend on that also. Since there are many laminae, $T(\Delta T)^2$ would always be small compared with T^3. Arithmetical illustrations could be given but the above shows that the effect of the rate of heat flow would be small in itself and moreover that it would be entirely masked by the rapidly increasing temperature coefficient of the conductance, varying as T^3.

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[1] Heat Transmission Engineer, U. S. Bureau of Mines, Pittsburgh, Pa. Recd. March 26, 1925.

In a cellular material the radiation factor part of the heat transfer will itself be small compared with the conduction factor, so that the ΔT effect will become insignificant.

Since there is apparently no other action that might account for the results obtained, it is more reasonable to look for test errors. Assuming the computations are correctly made, the most probable source of error would be the temperature measurements through the refractory, as all computations for conductivity depend on the shape of these curves. The errors in measuring the heat absorbed by the calorimeter should not be large and would only slightly affect the values here discussed. The measuring of temperatures by means of holes drilled in the direction of the heat flow is wrong in principle, has often been found to give inaccurate results, and has been used seldom. The use of the wires to give three sets of couples would add to the capacity to carry away heat from the couple points and lower their temperatures, and the passing of their wires through the metal of the calorimeter may possibly assist in the cooling.

An opposite action may have occurred due to hot gases passing through the thin layer of material at the hot end of the hole, or the two actions may have been combined.

Whatever may have been the cause, the temperature curves themselves, Figs. 6, 7, and 8, show very unlikely tendencies. Figs. 7 and 8 show a considerable and extended curvature when they pass from one material to another. The correct values would give sharply defined changes of slope, with some indication of the joint resistance. The humps in the curves of Fig. 6 indicate a large and rapidly accomplished change in conductivity at a comparatively low temperature which would have to be accounted for. Curve 1 of Fig. 8 shows an even larger change at a still lower temperature.

If these curvatures are not justifiable, then the slopes of some other part of the curves must be changed to take them out, and such alterations might do away with the differences due to rate of flow.

The above are of course only suggestions and surmises, and one would never deny the possibility of some previously unknown action being discovered. It does seem improbable, however, that such large departures from normal actions should be confined to one material, without some indication of it being previously noted in others.

The summation of these variations with heat flow are shown in Fig. 13; from these it is to be concluded that with small rates of heat flow the conductivity approaches zero, that is, the material tends to become a perfect heat insulator. In heating up a material the rates of flow must be small before they can become large, and therefore the logical conclusion would be that, since they could never start to transmit heat, they would never heat up, or would do so very slowly if the conductivity tends to approach, but does not reach zero.

M. L. HARTMANN AND O. B. WESTMONT:[1] In reply to Mr. Nicholls' discussion, further work is in progress to confirm our conclusions that the apparent thermal conductivity of refractories at high temperatures does change with heat flow. There exist so very few reliable thermal conductivity data on walls transmitting varying amounts of energy (especially at high temperature) that no one is warranted in categorically denying the possibility of a change of apparent thermal conductivity with variations in heat flow.

Before starting this investigation we made a thorough study of the possible methods of measuring the conductivity coefficient at high temperatures and concluded that the one employed by Dudley was the most accurate and at the same time most practical for use under actual operating conditions. A casual examination of the discordance of the results of previous investigations is sufficient to justify the adoption of this method in preference to those used by the earlier investigators.

The use of thermocouples for measuring the temperature gradients is undoubtedly the most accurate method. It is true that these couples do conduct some heat, but this does not affect the results appreciably. Regardless of the position of the wires relative to the direction of heat flow in the test wall, it is evident that practically the same amount of heat would be carried away by conduction through the couple wires.

The curvatures in Figs. 6, 7, and 8 at the wall joints and near the calorimeter are due to inaccuracies in measuring surface temperatures at joints. So many factors, such as surface irregularities, local convection currents, etc., affect the temperatures at joints and surfaces that we expected "unlikely tendencies" and consequently did not use the data in our calculations on furnace walls. Because there are recognized inaccuracies in these joint measurements, there is no justification in assuming a similar error in the measurements in the major portion of the test wall.

In using either fixed or movable couples for measuring the temperature gradient there is a certain temperature differential between the interior of the solid brick and the junction of the thermocouple, but this differential is constant. Since it is constant at different positions the slope of the gradient curve is realized and we have an accurate basis for calculating the thermal conductivity. In using fixed couples for measuring gradients, either a prohibitive number of couples would be required or assumptions have to be made that the gradient is uniform between the couple junctions.

The portion of the curves near zero in Fig. 13 indicate the trend of the thermal conductivity-heat flow curves. These curves, however, should not have been drawn through the zero point, and may be accurate only so far as the last indicated observation.

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[1] Recd. April 7, 1925.

QUANTITATIVE DETERMINATION OF THE DEVELOPMENT OF MULLITE IN FIRED CLAYS BY AN X-RAY METHOD[1]

By Louis Navias

ABSTRACT

Firing clays alone or with fluxes to high temperatures results in the formation of mullite crystals in a highly siliceous vitreous mass. Quantitatively, the extent to which mullite in clays is developed by firing to cone 10 has been determined for Ivory Fat English ball clay, Great Beam ball clay, Jernigan Tennessee ball clay, M. & M. English ball clay and A-1 English china clay.

The method consisted in procuring X-ray patterns by the powder method of the clays fired with feldspar as a flux, using mullite as a reference material. The intensities of the lines in these photographic films were then compared with the intensities of lines obtained from a series of mullite and feldspar mixtures, fired to vitrify the flux.

The results given in Table II indicate that each clay develops the maximum quantity of mullite in crystalline form, which the chemical composition of the clay allows.

Introduction

At the present time the fact is fairly well established that heating a clay to high temperatures results in the formation of the crystalline compound, *mullite*,[2] the aluminum silicate, $3Al_2O_3.2SiO_2$, which in former days was erroneously considered and recorded as sillimanite. Mellor and Holdcroft[3] maintained that the formation of sillimanite in kaolinite when heated over 1200° was due to the recombination of the free alumina and free silica formed at about 500°. Vernadsky[4], however, believes that a kaolin at 420–530° forms an anhydride $Al_2Si_2O_7$, leverrierite. After polymorphic changes at higher temperatures the nucleus at 930–950° breaks up during an exothermic reaction setting free SiO_2. It is not the province of this note to deliberate on these different views other than to indicate that at these higher temperatures a crystalline aluminum silicate is formed. With our present knowledge of the subject it is safe to assume that the compound is *mullite*.

More recently Kraner[5] has followed the development of mullite in fired clays by means of the changes in refractive index of the aggregates of material resulting from heating the clays to successive temperatures. The keynote to his paper is contained in the sentence "Because we cannot see crystals of sillimanite in the (clay) mass is not sufficient cause to state that submicroscopic or colloidal crystalline sillimanite is not present." His conclusions in part are:

"Sillimanite development seems to be a gradual rather than a sudden one.

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb. 1925. (White Wares Division.)

[2] N. L. Bowen and J. W. Greig, *Jour. Amer. Ceram. Soc.*, **7** [4], 238–54 (1924).

[3] J. W. Mellor and A. D. Holdcroft, *Trans. Ceram. Soc.* (Eng.), **10**, 94–120 (1910–11).

[4] W. J. Vernadsky, *Trans. Ceram. Soc.* (Eng.), **22**, 398–401 (1922–23).

[5] Hobart M. Kraner, *Jour. Amer. Ceram. Soc.*, **7** [10], 726–34 (1924).

With progressive heating it probably begins as soon as the clay molecule is dehydrated."

"Sillimanite development apparently takes place as abundantly in clays which do not contain impurities as in those in which early fluidity operates to promote the size of crystals."

Apart from the theoretical interest in the subject of the development of mullite in clays, or in compositions which contain clays, there is also the practical aspect which would benefit from a solution of the problem of the extent to which mullite is developed in fired clays. Searle[1] states that "Ideal porcelain should consist of a mixture corresponding to the formula $Al_2O_3.SiO_2$ (sillimanite) and a fusible glass which binds the other particles firmly together. When materials capable of producing such a mixture are heated to a sufficiently high temperature they will form a felted mass of sillimanite needles bonded with a glass cement." Aside from the plasticity necessary for working a porcelain composition it is important to know whether a ball clay contributes as much as a kaolin to the fired product with regard to the development of mullite as interlocking crystals, and whether individual clays of any type may be classified according to this property.

As will be shown later, resulting from the molecular transformations which a clay undergoes in firing there is left in the magma a superabundance of (free) silica. And there is some justification in Reichau's[2] remark that "silica in a (porcelain) body does not aid, but actually prevents the growth of sillimanite......," in criticizing Searle's[3] statement "the chief purpose of the clay and some of the free silica in all porcelain is to produce the felted mass of sillimanite crystals, which form the skeleton of the finished ware and to provide a reinforcement which will prevent undue distortion of the ware."

Our purpose was therefore to obtain some quantitative evidence of the extent to which mullite is formed in fired clays, and especially in combination with a flux like feldspar, somewhat simulating conditions obtained in practice. The method was that of making direct comparisons between a set of standards containing known percentages of mullite and fired clays containing unknown quantities of mullite, by means of the intensities of the mullite pattern obtained on photographic films by exposing the materials to X-rays.

Historically it is interesting to note Zoellner's[4] results. By heating clays to high temperatures and then disintegrating the products in hydrofluoric acid, he obtained a residue of mullite crystals. He concluded that cone 10 (ca 1300°) had to be reached before the mullite could be obtained, and that the plastic clays gave only 3–5% mullite whereas the lean clays (kaolins) gave 25% under similar conditions of firing.

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[1] A. B. Searle, "The Chemistry and Physics of Clays." London, 1914, p. 375.

[2] K. H. Reichau, *Keram. Runds.*, **38,** 1–26 (1924).

[3] A. B. Searle, *loc. cit.*, p. 377.

[4] Zoellner, *Brit. Clay Worker*, **22,** 40 (1913).

Materials Experimented With

Mullite Mullite was prepared in quantity by fusing pure silica and alumina in the correct proportions to give $3Al_2O_3.2SiO_2$. The raw materials were well mixed and placed in a flat rectangular sagger. An arc was struck between two large graphite electrodes imbedded in the mixture, whereby the mass at the center was fused. The electrodes were moved apart until the resistance to the current became too great to maintain the arc. After cooling, the fusion was removed. It consisted of a large cake of crystalline material surrounded by unfused and partially fused batch. The latter was removed by grinding, yielding a mass of mullite crystals, some over an inch in length. Microscopic examination of a thin section, and of the powder of the inner mass revealed the needle structure and optical properties of mullite. After a few trials, products free from glass were easily obtained.

Clays The clays experimented with are given in Table I, with chemical analyses determined on three of the samples. The analysis of the M. and M. ball clay is an approximate one supplied to us by the producers of the clay. The chemical analysis of the feldspar is also included.

TABLE I

CHEMICAL ANALYSES OF CLAYS AND FELDSPAR

	Jernigan Tenn. ball clay	Ivory fat Eng. ball clay	M. and M. Eng. ball clay	A-1 Eng. china clay	Derry feldspar
SiO_2	50.80%	54.62	51.55	42.10	63.82
Al_2O_3	27.75	25.32	30.70	38.83	20.50
Fe_2O_3	1.95	1.62	2.33	0.81	..
CaO	0.40	0.62	0.47	0.56	0.50
MgO	0.88	0.95	0.20	0.66	0.61
K_2O	n.d.	n.d.	1.40	n.d.	11.05
Na_2O	n.d.	n.d.		n.d.	3.59
Ign. loss	17.80	16.20	13.37	17.28	0.40
	99.58	99.33	100.00	100.24	100.47
Mol. ratio $\frac{SiO_2}{Al_2O_3}$	3.11	3.66	2.86	1.84	

Clay Series The clays were fired to cone $9^1/_2$ in a commercial kiln, and pulverized for X-ray examination.

Clay-Feldspar Series Each of the clays in the raw state was mixed with feldspar in the proportions of 60 parts clay and 40 parts feldspar, made into cones and fired in a commercial kiln to cone $10^1/_2$. A pulverized portion of every fusion was taken for the comparisons. The feldspar and clay in each instance had vitrified, and microscopically the only crystalline materials present were mullite crystals developed from the clays during the heating and cooling, and the quartz fragments introduced as an impurity.

Mullite-Feldspar Series Mullite, finely ground was mixed with feldspar in proportions of 0, 5, 10, 15. . . .50% and made into cones which were fired to cone $9^1/_2$. The feldspar fused to a glass and did not attack the mullite appreciably. The resulting fired cones were ground to powders to form a series of mullite standards from 0 to 50% with feldspar glass as the diluent. The quartz content of the feldspar was less than 1%.

Experimental Procedure

Clay Series One-half of a fine capillary glass tube having a partition at the center was filled with the powdered fired clay mixed with an equal volume of flour, and the other half with powdered mullite mixed with an equal volume of flour. The flour merely separates the particles and dilutes the material. Each tube, with a photographic negative held in an arc of a circle behind it, was then exposed to X-rays[1] for 165 hours. In this manner a photographic film was obtained on which the lines on the upper half represent the crystalline materials in the clay, whereas the lines in the lower half are representative of the reference substance, *mullite*.

In all cases the fired clays gave intense X-ray patterns identical with that of mullite, indicating that they all contained large quantities of mullite. However, the lines were too intense to enable a comparison to be made of the relative contents of mullite in the different clays.

Clay-Feldspar Series By a similar process, X-ray patterns were obtained of the clay-feldspar series, with the mullite as the reference material in each case, each sample having been diluted with flour. Again the only pattern obtained for each of the clays was that corresponding to the mullite. Under the conditions of exposure to X-ray there was no evidence of any quartz lines on the films, although quartz was known to be present in the ball clays.

Mullite-Feldspar Series Each of the mullite-feldspar series containing from 0 to 50% mullite in increments of 5% was treated as an unknown. The reference substance mullite was mixed with flour. Every photographic film thus contained in the upper part the lines due to the mullite diluted with feldspar, and in the lower part the lines of the pure mullite. The intensities of the more prominent lines of the pattern increase as the percentage of mullite in the series becomes greater, and there is no difficulty in detecting differences of intensity between them. The film of the 100% feldspar was blank except for a few extremely faint lines corresponding to the small quantity of quartz present.

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[1] For details and principle of power method see article in *Gen. Elec. Rev.*, 1925, by W. P. Davey.

Quantitative Determination of Mullite Content in Fired Clays

A direct comparison was then made between the ratio of intensities of the two sets of lines on a clay-feldspar film with the ratio of intensities of the two sets of lines on each of the films of the mullite-feldspar series. Where the relative intensity of the unknown lay clearly between two standards an average value was taken. For every match of intensities a simple calculation gave the percentage of mullite contained in the respective clay. The quantity of mullite developed in each fired clay calculated as a percentage of the raw clay is listed in Table II under the heading "Mullite determined."

At first appearance the percentage quantities seem rather large. It is then interesting to compare the percentages of mullite thus found in the fired clays with the maximum percentages of mullite which can theoretically be found from the alumina and silica contents of the clays. The calculated values are given in the column headed "Mullite calculated" and are based on the chemical analyses of the raw clays.

Within the estimated experimental error of about ±5% the calculated and determined values agree surprisingly well and they lead to the interpretation that the clays experimented with whether ball clay or china clay when fired to cone 10 (about 1300°) develop in a crystalline form the maximum quantity of mullite which their alumina and silica contents will allow. Notice should be taken of the fact that two of the ball clays developed only half of the mullite accredited to the china clay.

TABLE II

MULLITE DEVELOPED IN CLAYS FIRED TO CONE 10

	Molecular proportions			
	Al_2O_3	SiO_2	Mullite calculated	Mullite determined
Ivory Fat Eng. ball clay	3.00	10.98	35%	33%
Great Beam ball clay	..	..	..	33
Jernigan Tenn. ball clay	3.00	9.33	38	40
M. and M. Eng. ball clay	3.00	8.58	43	50
A-1 Eng. china clay	3.00	5.52	54	60
Mullite	3.00	2.00	..	..

The values are given as weight percentages of the respective raw clays.

To show the great excess of silica that must necessarily remain in the magma the silica-alumina ratios of the clays have been calculated on a basis of $3Al_2O_3$ to have a common term with the mullite formula. In the china clay the excess of silica is about 4 moles, whereas in the ball clays the excess silica varies roughly between 6 and 9 moles. With so large an excess of silica present, it is to be expected that at higher temperatures and in the presence of fluxes, partial solution of the mullite will take place, and as the excess of silica becomes greater the quantity of mullite remaining in the cooled magma will be correspondingly decreased. This condition will become more pronounced when silica is added to the composition, as for example, quartz or flint in porcelain. The development of a crystalline phase is intimately connected with the viscosity of the magma and the presence of large quantities of silica in the mixture, will tend to inhibit the crystallization of mullite on account of the increasing viscosity as the silica dissolves in the melt.

By a rational analysis the Ivory Fat English ball clay was found to contain 15% free quartz, leaving 36% SiO_2 combined with 28% Al_2O_3, thus giving a silica-alumina molecular ratio of 2.2. Old analyses gave, on discounting the free silica, molecular ratios of 2.1 for the Ivory Fat English ball clay, and 2.0 for the M. and M. English ball clay. The A-1 English china clay on the other hand was practically free from quartz and had a molecular ratio of roughly 1.8. A review of the literature shows similar proportions for washed clays and for clays whose chemical analyses specifically state the free silica content. In the former the free silica has been removed, while in the latter allowance can be made for the free silica.

The TiO_2 and Fe_2O_3 content of a clay is another factor which cannot be overlooked in a study of the subject. Bowen, Greig and Zies,[1] have shown that the inclusion of these oxides in the composition of the mullite affects its optical properties. It would seem plausible then to assume that these oxides combine with silica and add their quota to the total mullite, crystallizing out.

With the extreme variations of the silica-alumina molecular proportions of 1.8 and 2.2 calculation shows that a clay with the smaller ratio can develop 68% mullite, whereas the clay with the larger ratio can develop 61%, these percentage values being based on the alumina and silica contents only, which will apply to fired clays that contain no other oxides. The difference of 7% mullite obtained between these wide limits is small. While no generalizations on this point are intended it is striking how closely the argillaceous substance in each of the clays approaches in composition the theoretical molecular proportions of kaolinite, and how small an effect the above-mentioned variations have upon the maximum development of mullite in the respective clays.

Conclusions

1. By comparing the X-ray patterns obtained from clays, fired either alone or with feldspar as a flux, with the X-ray pattern of mullite it is found

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[1] Bowen, Greig and Zies, *Jour. Wash. Acad. Sci.*, **14,** 183–191 (1924).

that the crystalline development in the fired clays is similar to the crystalline compound mullite.

2. The extent to which the mullite is developed in the clays fired to cone 10 has been determined quantitatively, the values being 33, 33, 40 and 50% for the ball clays and 60% for a china clay, calculated as weight percentages of the raw clays.

3. By calculating the theoretical quantity of mullite which each clay can develop from its alumina and silica content, and comparing these calculated values with the quantitatively determined values of mullite, it is shown that within the experimental error each clay, whether a ball clay or china clay develops the maximum quantity of mullite, theoretically possible.

4. From the limited number of clays experimented with it appears that there is only a small difference, if any, between the clay substances of the china clay and the ball clays, the criterion being the development of mullite on firing.

Acknowledgments

The writer wishes to express his thanks to A. W. Merrick for the preparation of the mullite, and to W. P. Davey for the X-ray work.

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A METHOD OF CONTROL OF ENAMEL FOR DIPPING FLAT WARE[1]

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ABSTRACT

Development of varying specific gravity to control the dipping consistency of ground coat. The necessity of constant mill load and milling. Most efficient milling reached when $^1/_2\%$ of glass was retained on 150-mesh screen.

The object of the tests is to develop a practical method of control of the dipping operation on flat ware. Such a method must be one which can be readily introduced into the shop for quick and practical results. As the ground coat enamel is the first as well as the most important coat to be applied to the steel, experiments were made with this enamel and with favorable results.

Standards, whereby enamel shops may govern their various products, operations, etc., have long been sought by the enameler and it is quite possible that the experiments and the results thereof described in this paper may be beneficial.

In attacking the problem of control of our dipping and draining, our object was to secure a method of controlling the enamel at the dipping tubs, whereby a uniform thickness of coating of enamel could be secured day after day, and a method of control of the milling operation which would deliver a uniform enamel to the dipping tubs.

Since heavier or thinner enamel is secured by adding at the tubs either heavier enamel or water, we decided it would be feasible to control the dipping consistency by specific gravity determinations or weights per unit volume.

Throughout this investigation a standard mill charge was used in each instance mentioned and consisted of the following:

1000 lbs ground coat frit
100 lbs. ground flint
60 lbs. clay
10 lbs. borax
2 lbs. soda ash
water

To vary the specific gravity water was added to our standard slip as it came from the mill, and weights taken of a constant volume for variations

Table I

Number	Pounds per liter	Appearance after firing
1	3.98	Too thick
2	3.89	Too thick
3	3.85	Good
4	3.79	Thin
5	3.75	Thin. Started to fire out
6	3.71	Fired out

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb., 1925. (Enamel Division.)

in the water content; trials were then dipped in the various samples and fired with the results as given in Table I.

The results of these trials indicated that the enamel used was milled finer than necessary. Another mill was therefore started and samples drawn from the mill at various times. Screen analyses of these samples were made with the following results.

TABLE II

PER CENT OF GLASS RETAINED ON SCREENS

Milling time, hrs.	Mesh 150	120	100	80	60
12	14.56	9.88	5.36	0.90	0.18
14	10.77	5.60	1.79	.26	.07
16	7.04	4.03	.86	.14	.02
18	4.98	3.01	.64	.12	.01
20	3.16	1.73	.25	.02	...
22	2.02	.87	.13	.01	...
24	1.39	.68	.07	...	...
26	.97	.42	.04	...	...
28	.70	.26	.02	...	...
30	.47	.16	.06	...	...
32	.29	.12	.01	...	...
34	.19	.07	.01	...	...
36	.12	.04	...	...	...

A sample of this slip was dried and found to contain 25.23% water.

Samples from the above milling were made up to a weight of 3.85 lbs. per liter, trials dipped in them and fired with the results shown in Table III.

TABLE III

Milling time, hrs.	% loss by drying	Lbs. per liter	Appearance after firing
16	28.64	3.85	Fair. A little too thin
20	28.97	3.85	Good. A little thin
24	29.17	3.85	Good. Correct thickness
30	29.25	3.85	Fair. A little thick
36	28.91	3.85	Poor. Too thick

Since we had secured the best results with our standard mill charge when run from 20 to 24 hours, and had found it necessary to add a certain amount of water to this enamel in order to secure the weight of 3.85 pounds

TABLE IV

PER CENT OF GLASS RETAINED ON SCREENS

Milling time, hrs.	Mesh 150	120	100	80	60
14	3.59	1.63	0.28	0.06	0.03
16	2.19	.83	.13	.03	.01
18	1.19	.47	.07	.01	...
20	.78	.26	.02	.01	...
22	.42	.13	.02	...	...
24	.28	.07	.01	...	...

per liter, we decided to run another mill trial in which the necessary water was added to our standard mill charge in order to bring this enamel to an approximate weight of 3.85 pounds per liter. The results of the screen analyses of this trial were as shown in Table IV.

Trials were dipped in the samples drawn from this mill at the various times as shown in Table IV, all of which had a specific gravity of approximately 3.83 pounds per liter with the results as shown below (Table V).

TABLE V

Hours, milling	Appearance of fired trials
14	None made—enamel too thin
16	Fair
18	Very good
20	Good
22	Good—thick
24	Good—thick

The degree of fineness of the frit in suspension has a decided influence on the thickness of the enamel which will adhere to the ware in draining when all other factors are constant.

Separate mills of enamel gave like results when the per cent of glass retained on the same mesh screen was the same, or nearly so, for the separate millings at the same specific gravity.

Variation of the specific gravity of a particular slip varies the thickness of the enamel coating which will adhere to the ware.

It will be noted from a study of Tables II and IV that approximately the same degree of fineness was secured in 18 hours with a water content of about 29% as was secured in 24 hours with a water content of 25%. Further study of these tables indicate a rather sharp decrease in the grinding action of the mill after a certain degree of fineness is attained. This point is more clearly shown by the accompanying curves (Fig. 1).

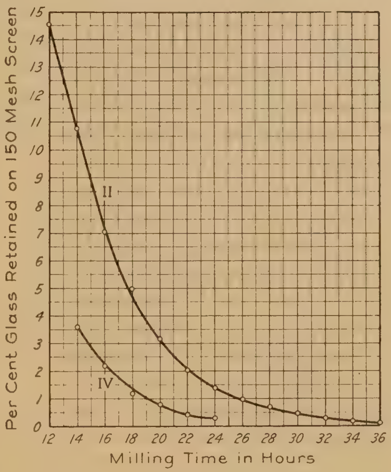

FIG. 1.

In applying the above data to our shop practice we have standardized oug mill charge and milling with satisfactory results. All water, glass, clay, etc., introduced in the mill charge is accurately weighed and our actual milling put under control by use of a revolution counter. The degree of fineness is frequently checked by screen analyses. The specific gravity of the enamel is daily brought to the standard set before any ware is dipped and after every addition of enamel to the tubs, with the result that we have almost eliminated our difficulties due to uneven dipping.

In setting the enamel the foreman is provided with a narrow mouthed glass stoppered bottle (quart size). Each bottle is calibrated according to its volume, as compared to one liter. The foreman does the weighing and knows that for the particular bottle which he is using, the bottle filled with the slip he is going to use must weigh just so much for good dipping. He adds either water or heavier slip in order to get the slip to the required weight.

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GLAZES COLORED BY MOLYBDENUM[1]

BY WAYNE E. BARRETT

ABSTRACT

Molybdenum used as a colorant for glazes has a strong coloring power even though used in small percentages, affecting the glaze as R_2O_3. Both a bright yellow and a bluish green were secured.

Molybdenum has a strong coloring power. The oxide was mixed in the porcelain batches. These turned a deep blue on drying in the plaster molds. When fired to cone 12, the samples had a bluish green color, and though both 1 and 2% were used, there was no apparent difference in the intensity of the color. Different percentages of oxide of molybdenum were added to a bright and to a matt glaze without grinding. The test pieces were white hexagonal underfired tile. The color secured was a bright yellow.

BODY

Tenn. ball clay	38%	
Feldspar	29.5%	
Flint	32.2%	
MoO_3	2 and 3%	Cone 12

GLAZES

Bright			
0.10 CaO			
0.20 K_2O	0.25 Al_2O_3	1.6 SiO_2	Cone 02
0.70 PbO			
Matt	2, 4, 6, 10% of MoO_3 added to each		
0.45 CaO			
0.20 K_2O	0.29Al_2O_3	1.87 SiO_2	Cone 2
0.35 PbO			

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[1] Presented at the Annual Meeting, AMERICAN CERAMIC SOCIETY, Columbus, Ohio, Feb., 1925. (Art Division.)

THE ACTION OF ARSENIC COMPOUNDS ON TANK BLOCK[1]

By D. J. McSwiney

ABSTRACT

Comparison of the average life of soda lime glass tanks melting green glass and those melting flint glass in which selenium is used as a decolorizer, where the same or similar batch and operating conditions obtain in both cases, shows that the life of the selenium flint tanks is invariably much shorter than that of the green tanks. This shortening of tank life is independent of the amount of selenium used or the form in which it is used but varies with the amount of arsenic used in conjunction with the selenium.

A much discussed point in connection with the use of selenium as a decolorizer for soda lime flint glass is the effect of the decolorizer on the life of the tank in which it is used. Most flint glass manufacturers claim that by the use of selenium the life of their tanks is greatly reduced. In answer to this the counter claim is made[2] that decreased tank life through the use of selenium is only apparent; that the decreased life is actually due to the increased pull exerted upon the tanks through the introduction of high speed glass forming machinery during the past decade, and through the higher temperatures and more fusible and corrosive glasses used to meet this increased pull.

This may possibly be true of glass tanks in general, but it is none the less true that the life of selenium flint tanks has been abnormally shortened, as is evidenced by the fact that in any factory where green and flint soda lime glasses are made and in which the flint glass is decolorized by the use of selenium and arsenic, the life of the green tanks is, on an average, from 50 to 100% greater than that of the flint tanks, although, the same block is used in the two tanks; they are warmed in the same way, the same temperatures are used, the same average pull, and the batch is the same with the exception of the selenium and arsenic used for decolorization. Moreover, in those cases where the introduction of high speed forming machinery antedated the change from manganese to selenium, the same condition holds—the average life of the manganese tanks was much greater than the life of selenium tanks operated under similar conditions with a batch which was probably more corrosive than the present selenium batch in which little or no niter is used.

The Case of Selenium

The type of attack of the present selenium batch differs from that of the old manganese batch. The action of the latter was exerted on the block in the vicinity of the dog-house and on the rear walls; while the action of the selenium batch appears to be an accentuation of the erosive action of the glass, being exerted largely on the points where the rate of glass flow is greatest, that is on the throat and the block in the working end near the troughs. The blame for this increased action has always been put on the selenium as this was the only new glass material introduced, and this despite the fact that there was no particular evidence that selenium should have such a corroding action. The amount of selenium introduced into the glass for decolorization never exceeded 0.003%; in cases, such as selenium ruby, where four hundred times this amount of selenium is used there is no evidence of increased block or pot attack; the degree of corrosion does not appear to be influenced by the form in which the selenium is introduced and is independent of the amount of selenium used for decolorization.

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb., 1925. (Glass Division.)

[2] R. R. Shively, *Bull. Amer. Ceram. Soc.*, **3** [9], 333 (1924).

I have long felt that the corrosion should be ascribed, not to the presence of selenium in the glass, but to the use of the arsenic oxide, and an investigation of the problem from this viewpoint affirms this assumption.

Corrosion in Proportion to Arsenic Content

While the increase in corrosion of flint tanks over that of green tanks in the same factory and operated under the same conditions does not vary as the amount of selenium used for decolorization, it does vary as the amount of arsenic so used. The selenium tanks which show the greatest average decrease in life are always those in which the greatest amount of arsenic is used. Those flint tanks using selenium as a decolorizer but which do not use arsenic in conjunction with it, show no decrease in average life over similarly operated manganese or green tanks, except where such a decrease can be easily attributed to a radical change in batch or operating conditions. Some flint tanks using selenium without arsenic show an apparent average increase in tank life. In the case of one glass manufacturer, when selenium was first used in his batch as a decolorizer it was used without arsenic, and for a period of three years following such introduction the average life of his flint tanks was about the same as his green tanks operated under the same conditions. To eliminate the brown selenium color four pounds of arsenic per ton of sand was then used in the batch and during a period of almost three years the life of his flint tanks decreased to an average of about eight months compared with an average of twelve months for the green tanks over the same period.

The effect of the arsenic on the block is not limited to flint tanks but can be seen in green tanks using arsenic. For example, a green glass manufacturer using a high grade sand changed to a local sand containing titanium, and to eliminate the off-color caused by the titanium, he used five pounds of arsenic per ton of sand in his batch. The average life of his tanks dropped from fourteen months without arsenic to about six and one-half months with arsenic. As the cost of the arsenic offset the decreased cost of the local sand he returned to the use of the former sand and his tank life increased to about eleven months.

The use of arsenic in glass batches is not new, as it has long been used in glass as a clarifying agent, especially in colored glasses. However, its use in such cases was more or less isolated and fair comparisons could not readily be made. The first time arsenic was consistently used and in such a manner that comparisons of its effect could readily and fairly be made was in its use in conjunction with selenium for decolorization. It is, moreover, a general belief among glass makers that the small amount of arsenic added to the batch is completely volatilized from the glass early in the melting process; if such were the case, it would be difficult to see how the arsenic could affect the block near the working end of the tank. That the arsenic is not completely volatilized from the glass is evidenced by the effect which it exerts on the selenium color not only during melting but during the entire period the glass remains subjected to heat. Moreover, numerous published examples of glass analyses show the presence of varying amounts of arsenic in the glass. To endeavor to find about what is the ratio of the amount of arsenic remaining in the glass to the amount added to the batch, I examined two samples of soda lime glass, one taken from in front of the dog-house about eighteen inches below the surface, and the other taken from in front of the throat. The batch from which the glass was made contained about three pounds of arsenic per ton of sand. Analysis of the dog-house sample showed that 65–70% of this amount remained in the glass and the throat sample showed that 45–50% remained. Considering the length of time the second glass must have been under the action of heat, it would indicate that the arsenic compounds present must be quite stable to glass mixtures at melting temperatures. It is probable that the arsenic is present in the form of sodium arsenite.

It is not very clear why the presence of these arsenic compounds should exert a corrosive action on tank blocks, but it would appear from the above evidence that such an action does take place. As the glass sinks toward the throat and slowly cools, part of the arsenic compounds which in the upper hot layers remained dissolved in the glass, slowly separates out of solution, and it is this separated material which exerts the corrosive action on the throat. Relatively small amounts of salt cake can cause a considerable increase in the attack of the glass on the block and it is possible that the action of the arsenic compounds is similar but is more intensive due to the evident greater stability of the arsenic compounds to the action of glass at melting temperatures and to a slower rate of volatilization. The amount of arsenic remaining in the glass will not be constant, but will depend greatly on the oxidizing or reducing conditions which obtain in the batch and tank.

1689 W. Third Ave.
Columbus, Ohio

A SLIP PAINTING PROCESS SUITED TO THE CRAFTSMAN WHOSE EQUIPMENT IS LIMITED[1]

By D. W. Cox

ABSTRACT

The raw materials of the common stoneware business are used. The temperature needed is that of the maturing point of Albany slip, or cones 6 to 9. The kiln should be one designed to stand up under rather high temperatures. The ware is essentially once fired common stoneware decorated with a slip painting process.

Introduction

Common stoneware clays are those most often offered to the teacher and craftsworker by the potteries willing to supply prepared clay. Such clays seldom mature to the proper density when used with the matt and clear glazes generally used in schools and studio potteries so that leaking vases result. The process here described has the merit of overcoming this trouble, there is no crazing, and being fired only once, labor is saved for the craftsworker.

Equipment

The kiln should be one guaranteed by the manufacturer to stand up well under the temperatures necessary to mature glazes demanding cone 9, and better yet, one designed to use for hard porcelain work up to cone 18 if need be.

The ware are best formed on the potter's wheel.

A cheap air brush outfit such as sign writers use, or even the mouth spray used in charcoal drawing work, a few good camel's hair brushes, and a few orange wood modeling tools comprise the equipment, together with the wheel and kiln. The ware may, however, be built or modeled providing they are kept well softened at all stages of the work.

Technique

The process can best be described by giving the steps in a concrete example. The illustration herewith shown is of a vase made free hand on the potter's wheel, not turned down, but used as it came from the wheel. The handle is drawn, like a common jug handle. Since the whole work is that of men untrained in the fine arts the example is frankly the offering of the humble.

As is true with all slip painting done on the leather hard piece the artist must understand that work must either be done very rapidly or else work must be done in a rather moist room, with no drafts of air and with fre-

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[1] Received December 29, 1924. Presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, Feb., 1925. (Art Division.)

quent additions of moisture to the piece, which additions can best be done with the air brush. The softer the piece is while being painted the better the slip will adhere.

The example was decorated by first laying a ground of brown which is not very thick so that the buff gray of the stoneware body shows through it. The bulk of the slip added is white, but part of the decoration is made from the slip mixed with a good underglaze blue stain, while brown is mixed with part of the slip for other parts of the design.

The effect sought is that of early spring. Since the glaze used carries zinc oxide it is not possible to get either a pink or green. The craftsman, being untrained in ceramic chemistry, was forced to work with a very limited color palette, so that blue, brown and white and the natural color of the fired clay limited the colors possible.

After the ground is laid the slip is painted on and where desired is modeled.

When the piece is bone dry it is simply dipped all over in the glaze and the bottom is scraped clean of glaze, or in the terms of the potter the bottom is "fettled." The piece is then set into the kiln on its own bottom and fired to the proper temperature.

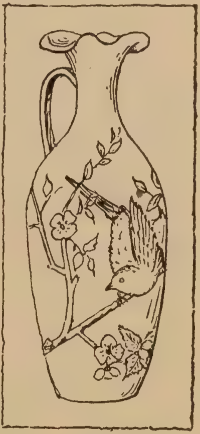

Fig. 1.

In the case of the example shown the firing was done in a commercial kiln, in about 48 hours. In the small portable kiln the firing should vary with the size of the piece but 18 hours should be about right. About 12 hours should be devoted to reaching cone 1 and the balance of the time from cone 1 on up to the maturing point, which will be not less than cone 6 and not more than cone 9.

Raw Materials Needed

Any prepared stoneware clay will probably work quite well. In the example shown the clay came from Brazil, Indiana, and is the clay from just below the block coal seam. The colors are the ordinary underglaze colors that can be had from any of the advertisers of such supplies whose names appear in the *Journal*. The raw materials for the slip can be had also from advertisers in the *Journal*.

The Slip

Feldspar	8
China clay	16
Ball clay	18
Flint	9

Use when of the consistency of tube paints.

THE GLAZE

Feldspar	53
Zinc oxide	10.5
Whiting	10.5
Flint	9
China clay	2
Ball clay	7

Use when weighing mixed with water 19.5 ounces to the pint.

Both slip and glaze can be prepared by soaking the weighed materials in plenty of water in stoneware jars over night, then mixing well with the hands and then passing the suspended mixtures through 60-mesh sieves. Allow the mixtures to settle and decant the surplus water, or else syphon off with a rubber tube. The slip will have to stand for some days before all the water can be removed and after that it should be allowed to stiffen slowly by evaporation until of the right consistency. When the slip is right it should be stored in sealed jars to keep it from drying out too much. The glaze will of course be rather thin, when the dipping is done.

If the experimenter will make use of glazes free from zinc oxide the color palette may be expanded. The process should work well in conventional decoration.

AMES, IOWA

SELECTION OF FIRE BRICK BY COMPARATIVE TESTS WITH A DETAILED DESCRIPTION OF THE METHOD USED TO MEASURE THE TEMPORARY EXPANSION OR CONTRACTION OF FIRE BRICK AT VARIOUS TEMPERATURES[1]

By F. A. Kohlmeyer[2]

ABSTRACT

This paper discusses the laboratory tests employed by the Electric Light and Power Company with which the author is connected, in selecting several brands of fire brick suitable for use in the construction of a power plant. A detailed description is given of the method used to measure the temporary expansion or contraction of fire brick at various temperatures and the procedure followed in the inspection of fire brick briefly outlined.

The testing and inspecting of fire brick by the purchaser has not until recently been given serious consideration. In fact it has been the demand of industries for refractories of a higher class and the difficulty of obtaining these which probably influenced many purchasers to determine for themselves the reliable sources of materials for their requirements.

It was the demand for a fire brick capable of withstanding a heavy load while under temperature as well as a brick which had a minimum tendency to spall, change its physical dimensions or collect slag while in service, which prompted the Electric Light and Power Company with which the author is connected to run laboratory tests upon about thirty brands of brick.

Description of Power Plant

A brief description of the powdered fuel furnaces in a new power plant which will have an ultimate capacity of 300,000 kw., should give an appreciation of the importance of selecting refractory materials of a high class for its construction.

The boilers are of the Stirling W. type and are designed for a steam pressure of 415 lbs. per sq. in. with a steam temperature of 700°F. The steam drums are 48 inches in outside diameter, with plates 2 inches thick. The heating surface of the boiler proper excluding the hearth screen boilers is 29,087 sq. ft.

The furnace is built with double walls, with air circulation through the intervening space tending to keep the wall cool and to warm the secondary air for combustion.

The height of the combustion space from the bottom of the furnace to the bottom of the center steam drum is about 60 feet. In plan the furnace is 23 x 34 feet and the furnace volume is about 25,140 cubic feet.

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[1] Recd. Dec., 1924. Presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, Feb., 1925. (Refractories Division.)

[2] Office of the Inspection Division, Purchasing Department, The Detroit Edison Co.

The Test Made on Refractories

The Company realized that a laboratory test could do no more than indicate several brands of fire brick most worthy of a thorough trial in actual service. Consequently at the completion of the tests, four brands of brick were selected which seemed best adapted to give the service required in the operation of the powdered fuel furnaces of this plant.

From the results of service tests to date we can say that the rating given the various brick in the laboratory has been quite accurate.

The tests conducted by the Research Department, of this Company, and particularly the method used in measuring the expansion of fire brick while under temperature, or temporary thermal expansion, will here be described.

1. Spalling The spalling tests were first conducted on all brands under consideration in order to eliminate the most undesirable brands from the more extensive tests which were to follow. In order to get comparative data on brick known to give different results in service, a few of the brands giving poor results in the spalling test were carried through the entire test schedule.

The spalling tests were conducted in a standard carborundum lined oil-fired furnace and in accordance with instructions of the American Society of Testing Materials (Serial Designation C38-21T). The alternate heating and cooling of each brick was repeated only 10 times, however, or until it broke across the face and the brick given a rating depending upon the loss in weight and the number of water dips it withstood. The loss in weight of a brick which broke during the test was considered as 100%. Four samples of each brand were used and the average result of the four taken as the value of the test.

2. Physical Dimensions Tests Ten brick of each brand were put face to face and were measured for total thickness, width and length.

3. Cold Crushing Strength This was obtained by testing three bricks of each brand in a standard type compression machine. The brick were placed in the machine in an upright position and the ends protected by asbestos pads to obtain an even bearing surface.

4. Hot Load Tests These were conducted, with the exceptions noted, as outlined by the American Society for Testing Materials (Serial Designation C16-20) using a furnace slightly larger than the standard test furnace specified, but similar in general design. Tests were run with loads of both 25 and 40 lbs. per sq. in. on the brick.

The brick was heated to 2462°F (1350°C) at the rate specified and this temperature maintained for 2 hours instead of $1^1/_2$ hours as is usually done. Care was taken to maintain an oxidizing atmosphere in the furnace as it was found that a reducing atmosphere appreciably affected the fusion temperature of certain brick under test.

The load of 40 lbs. per sq. in. was used, as brick in service in the large powdered fuel furnaces of the new power plant are actually under this load. The average result of three samples from each brand was taken as the result of this test.

5. Permanent Linear Expansion or Contraction Tests

These were run in the usual manner as outlined by the American Society for Testing Materials (Serial Designation C27-20) and it is therefore unnecessary to describe them. Three brick of each brand were used in this test.

6. Temporary Thermal Expansion Tests

A rather unique method was used to obtain the expansion of fire brick at various temperatures. It was considered important to obtain this information regarding the various fire brick under test as the temporary expansion indicates the probability of internal strains being set up in the brick on reheating, as well as the overall expansion of a wall made of these brick. The temporary expansion of fire brick is doubly important when these are to be used in the construction of furnaces as large as those in this plant where the furnace walls are over 60 feet in height.

A standard type of oil-fired testing furnace was used in determining the temporary expansion. This furnace was carborundum lined and equipped with a carborundum hearth to prevent an impingement of the flame on the brick under test.

The brick samples used for this test were those which had been previously used for determining the permanent expansion or contraction.

Two holes about 1/2 inch deep and 7 inches apart were drilled in the front top edges of each brick. Orton cones, having a fusing temperature well above that at which the furnace was to be run, were cemented upside down, into these holes with carborundum cement. The cones were placed so they projected about 1/4 inch above the face of the brick and the brick then placed in the test furnace previously described. The door of the furnace was bricked up and two 1-inch carborundum tubes placed horizontally so the Orton cones projecting above the top edge of the test brick were plainly visible to a person standing in front of the furnace and sighting through the tubes. The carborundum tubes, which extended from the face of the test brick and completely through the bricked-up door of the furnace, were employed to prevent a possible distortion of the line of vision due to the rapid movement of the hot gases.

A surveyor's transit was mounted on a substantial pier in front of the furnace in such a position that the Orton cones were visible through the carborundum tubes when sighting through the transit.

The transit was carefully leveled and the intersection of the vertical and horizontal cross hairs brought to focus on the inside top edge of one of the Orton cones. The telescope of the transit was then plunged or inverted through a vertical plane and focused on a steel scale mounted at such a distance from the transit as would give a suitable multiplication of the distance between the Orton cones. A diagram of the set-up is shown in Fig. 1.

By sighting on the Orton cone on the other end of the brick, plunging the telescope and obtaining another reading on the scale, two isosceles triangles were formed with the transit at the apex of each. The distance between the cones was the base of the smaller triangle, while that same distance enlarged and projected on the steel scale was the base of the larger triangle. Care was taken to see that the bases of these two triangles were parallel and that the steel scale was level.

In order to improve the accuracy with which readings could be taken, two movable trammels were mounted in such a position that their points just projected over the lower edge of the scale. The trammel points could then be set to coincide with the intersection of the cross hairs of the transit and the multiplied distance between the cones accurately determined on the scale. A magnifying glass was used to insure accurate scale readings.

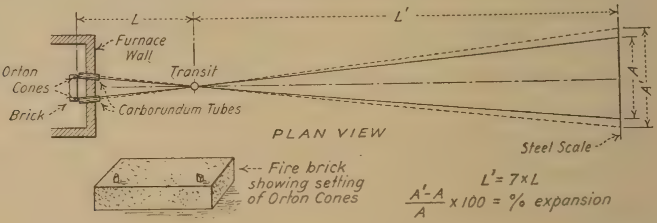

FIG. 1.

After obtaining a reading on the scale with the brick at room temperature, the brick was heated and the distance between the Orton cones, as multiplied on the scale, determined for both 2000°F and 2500°F.

Since the distance measured on the scale was directly proportional to the distance between the Orton cones mounted on the brick, the percentage of expansion could be calculated from the scale readings. The percentage of expansion was determined for both 2000°F and 2500°F and the average result of three samples of each brand recorded as the result of the test.

7. Brick-Cone Softening Temperature Tests

These tests were conducted as outlined by the American Society for Testing Materials (Serial Designation C24-20) using a standard type of gas fired testing furnace.

8. Coal-Ash Penetration Tests

These were run by filling 2 drilled holes in each brick to be tested with coal ash. The brick were then placed in a brick testing furnace and heated to 2500°F at the rate prescribed by the American Society for Testing Materials and maintained at this temperature for two hours. The brick were allowed to cool in the furnace and were then cut in two through the holes and an attempt made to determine the ash penetration. The results of this test were unsatisfactory as it proved to be difficult to determine the depth of ash penetration.

9. Coal-Ash Brick Cone Softening Temperature Tests

As the coal-ash penetration test was not conclusive, this additional test was made to determine the ability of the brick to resist the slagging action of coal ash.

It is clearly evident that the extent to which the fusion temperature of brick is affected when in intimate contact with coal ashes, measures their ability to resist slagging when in service in the boiler. This reaction, however, is chemical rather than physical and consequently some account must be taken of the coarseness of grind and porosity of the brick when considering the tendency to slag.

Cones were made of composite samples of the pulverized brick material to which were added coal ashes in varying percentages. The softening temperature of each mixture was determined on duplicate samples in the same manner as in the brick-cone softening temperature tests.

The results seemed to indicate that the slagging action of coal ash is due to the iron content of the coal. This conclusion was reached after using coals having both high and low percentages of iron.

While this test is chemical rather than physical, the results nevertheless were of considerable importance.

Inspection

The Inspection Division of the Purchasing Department of this Power Company is responsible for the inspection of all material bought on specification or otherwise subject to inspection.

In the case of fire brick, each shipment is given a visual inspection and if deemed necessary, checked for conformity to specifications by conducting tests similar to those outlined above.

If a shipment is not in accordance with specifications it is either rejected by the Inspection Division, or accepted provisionally dependent upon an adjustment between purchaser and vendor. This frequently takes the form of a price adjustment in conformity with the actual material received. At other times defective material received is replaced by the vendor.

It has been the experience of this Company that inspection actually pays on a plain debit and credit basis although the indirect savings are far more important.

The inspection and testing of fire brick has been beneficial in that it has resulted in locating several reliable sources of material. It has led to more efficient construction as well as more economical maintenance of boiler furnaces.

Inspection has also had an effect on the manufacturer of fire brick which is of great significance in that it has helped to force a development of the art.

An example will assist in illustrating this point. Several carloads of fire brick received by this Power Company from a certain vendor were flatly rejected as they were not within the specified and generally accepted tolerances for size. This action naturally led to some controversy, resulting, however, in the fire brick manufacturer voluntarily scrapping all of his old molds, dies, press boxes, etc., at a considerable expense.

Later the vendor frankly expressed his satisfaction at the results of this step, which judging from present developments toward the establishment of standard sizes in fire brick, would have been inevitable at some later date.

DETROIT, MICH.

Discussion

M. C. BOOZE:[1] At a time when fire brick specifications are becoming the vogue and greater attention is being paid to the quality of the refractories used than ever before, it is interesting to know that the standard tests can be used to distinguish between brick which give satisfactory and unsatisfactory performance in service.

It is unfortunate that comparative results are not given, especially on the coefficients of expansion, as there are few published determinations which were made at temperatures as high as those described in this paper.

To the writer, it appears that the use of the spalling test to eliminate some of the brands of brick from further tests is questionable. The use of powdered coal furnaces, such as described, is comparatively new in power plants and the performance of refractories in them has not been thoroughly studied. It seems, however, that rigidity under load and lack of shrinkage on the 9-inch brick would be of greater importance than spalling. The holding tile in the hollow wall construction should undoubtedly be tested first for spalling resistance, as they are comparatively large shapes.

Neither is it considered advisable to stop the spalling test at the end of ten dips. This would suffice to distinguish between brands which were good and bad in spalling properties, but would not show sufficient difference between some brands of first quality brick and the specially developed products which give exceptional spalling results.

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[1] Mellon Institute, Pittsburgh, Pa.

AN ELECTRIC FURNACE FOR SOFTENING POINT DETERMINATIONS[1]

By W. L. Pendergast

ABSTRACT

This paper presents a description of an electric resistance type furnace which has been designed at the Bureau of Standards for the determination of softening points of ceramic materials. The advantages claimed for this furnace are simplicity of design, with resultant low cost of manufacture and repair, economy in operation, high temperatures available, sufficient accuracy in determining softening points in terms of standard cones or actual temperature readings, and compactness of installation.

Introduction

A furnace to be used for the purpose of obtaining softening points, and which can be constructed in any plant having the facilities to fire clay products, is a desirable asset for plant control and would justify its installation by practically every concern manufacturing refractories because of its low initial cost and maintenance. Gas-fired furnaces have been adopted for this purpose, but their use is limited due to the difficulties encountered (1)in obtaining extreme temperatures while maintaining oxidizing conditions, (2) in determining these temperatures by means of the optical pyrometer and (3) in observing the cone plaque. High temperature gas furnaces also require compressed air, or gas, which, if not available, often necessitates the installation of expensive apparatus. Furnaces depending on electrical energy for heat seem to be the most easily adapted to designs for general and economical use.[2] Inductance types, and those using metallic resistors, are ideal, but the cost is generally prohibitive where temperatures required to fuse clays are to be obtained. For several years the Bureau has experimented with various carbon resistance furnaces, having in mind the development of a design which could be generally adopted by the ceramic industry.

Description of Furnace

A softening point furnace of simple construction, the parts of which are easily replaced, and which has given satisfactory service for the past two years in the ceramic laboratories of the Bureau, is shown in Fig. 1. This furnace consists essentially of a fire clay shell surrounding a carbon re-

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[1] Recd. Jan. 2, 1925. Published by permission of the Director, Bureau of Standards, U. S. Department of Commerce. Presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, February, 1925. (Refractories Division.)

[2] Samuel A. Tucker, *Electrochem. and Met. Indus.*, **5**, 227 (1907); A. Coggeshall and A. V. Bleininger, *Trans. Amer. Ceram. Soc.*, **10** (1908); W. Pip-Darmstadt, *Zeits. für Elek.*, **16**, 664 (1910); D. F. Calhane, *Sci. Amer. Suppl.*, **71**, 207 (1911); A. V. Bleininger and G. H. Brown, Bureau of Standards, *Tech. Paper* **7**; Liddell's "Handbook of Chemical Engineering," p. 478.

sistance element in which the heat is generated and which in turn surrounds a magnesite muffle. The trial cone plaques are placed in this muffle for test and in this manner are protected from reducing gases generated in the resistor. The entire furnace is enclosed in a sheet iron casing and mounted on an adequate stand.

The fire clay shell need not be of especially refractory material, but should resist spalling. This shell is simply a cylinder with three lugs to support the carborundum ring (*C*) shown in Fig. 2 and was pressed in a sheet iron mold. The shell rests on a fire clay disc (*A*) of the same material which is provided with a seating for the shell and the magnesite muffle. The carborundum ring (*C*) which is used to restrict the graphite electrode at the high temperature zone is made of a mixture of 95% No. 80 carborundum and 5% plastic kaolin, to which enough water is added to permit pressing into shape in a suitable mold. The magnesite muffle, seated in the fire clay base (*A*) and extending above the body of the furnace, is composed of four cylinders approximately equal in length and so placed that there is no joint in the zone of highest temperature. The individual cylinders are composed of the purest commercial electrically fused magnesite which is ground to pass a 20-mesh sieve and is thoroughly mixed with an organic binder (preferably gum tragacanth) and hand-rammed in steel molds. When dry, these cylinders can be easily handled and before being used should be fired as high as facilities will permit. It has been found advisable to make these rings as dense as possible and to fire them at least to cone 16 to prevent undue shrinkage and attack by carbon when in service. The current is introduced by means of copper electrodes (*G*), Fig. 2. These electrodes are copper bands 3 inches wide and $^{1}/_{4}$-inch thick, which are bent into a ring conforming with the inside diameter of the shell and provided with a lug, protruding through a slot, permitting the attachment of wire leads. These bands offer a considerable surface because of their shape and will be cooled automatically if the lugs are permitted to protrude at least 6 inches from the outside of the furnace.

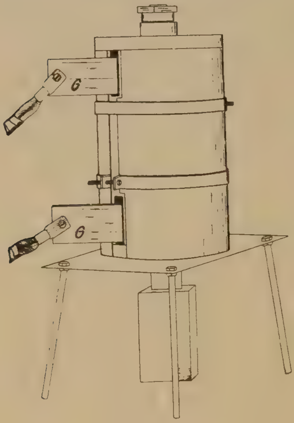

FIG. 1.

Having assembled the shell, base (*A*), the lower electrode, and the magnesite muffle, the space below the carborundum ring (*C*) is packed firmly with graphite or granular carbon. The ring (*C*) and the upper electrode are then put in place and the remaining annular space packed firmly with the material forming the resistor.

Care must be taken in packing the graphite evenly to obtain balanced resistance.[1] In this connection it should be noted that in this design the possibility of a hot zone forming has not been definitely overcome, but if care is observed in packing the graphite the operator can, after a little practice, obtain a resistor which will in practically every case function properly.

It should be noted that by using this design of electrode the graphite or granular carbon can settle while the furnace is being operated and still maintain satisfactory contact. The advantages of flake graphite over carbon grains have been demonstrated since, with the former, arcs in the body of the resistor were not as liable to be formed. After packing the resistor the refractory cover (*B*) is put in place. This cover should be ground to fit as accurately as possible to exclude air from the graphite. The fire clay shape (*E*) assists in concentrating the heat at the center of the muffle and serves as a peephole through which the cone plaque may be viewed. This shape (*E*) was made by grinding a fire clay tile to the proper dimensions. The upper opening of (*E*) is closed by laying a piece of No. 6 welding glass on a thin sheet of kieselguhr.

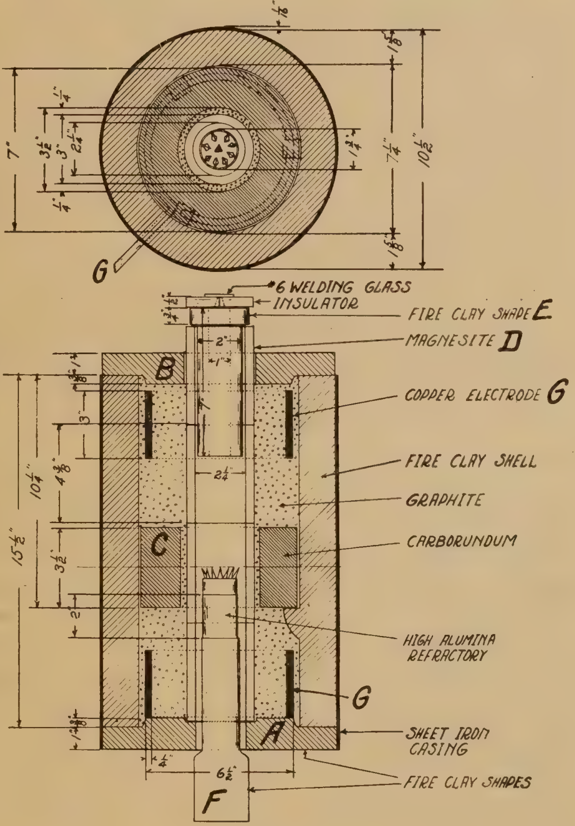

FIG. 2.

The cones are introduced from the bottom of the furnace and the plaque, usually made of a mixture of 50% calcined alumina and 50% plastic kaolin, rests on a base of the same material which in turn is supported by the refractory shape (*F*). This shape is made by so grinding a No. 1 refractory soap brick that when the shoulder is against the opening in (*A*) the cones are raised to the hottest part of the muffle, which is midway between the top and the bottom of the ring (*C*). This shape should not fit accurately in the opening, but permit a current of air to be drawn into the muffle during the operation. This current passes up through the hot zone and out at the upper end of the peephole (*E*), in this way replenishing the supply of oxygen in the muffle. The sheet iron casing which encloses the entire furnace provides the necessary added strength to the shell. The furnace is mounted on a stand as shown in Fig. 1 and can be placed on a table or wherever convenient.

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[1] O. P. Watts, "Granular Resistance Furnace," *Jour. Op. Soc. Amer. and Rev. Sci. Instruments*, 9 [6], 705 (1924).

Operation

In the operation of the furnace the introduction of the cones from the bottom has been found to be a decided advantage. This method eliminates the necessity of placing and removing cone plaques by means of tongs (which often results in the destruction of the test set) and permits the removal of the cone plaque as soon as the test cone has softened, which is a desirable asset. The saving of time is also an important factor since a new test set can be introduced conveniently without cooling the muffle below 1000–1200°C. If readings with optical pyrometers are desired, they can be obtained by mounting the instrument above the furnace and sighting directly on the cone plaque through a relatively small opening in the insulation.

Results shown in this paper indicate that the errors in temperature readings due to reflection and radiation are comparatively small and the readings sufficiently accurate for the purposes intended. In this work an optical pyrometer of the disappearing filament type was used. In using an instrument of this type the opening in the furnace through which the telescope is sighted must be large enough so as not to cut in on the cone of light rays required by the pyrometer, *i. e.*, the hole must be large enough so that the pyrometer telescope may be moved a little from direct alignment without affecting the apparent brightness of the furnace as viewed through the telescope and without affecting temperature measurements.

The furnace is operated on a 220 volt alternating current line through a 6 kw., 60 cycle, 220 volt primary, 47 volt secondary transformer. A ratio board is tapped in between the transformer and the furnace and cuts down the secondary voltage in steps of 20, 10, 8, 6, 2 and 1 volts. An ammeter with a capacity of 200 amperes is used in this circuit to assist in regulating the temperature and to prevent exceeding the capacity of the transformer.[1] This furnace, when connected with a 220-volt circuit having an 80% power factor and operated for seven hours, will consume 16.8 kw.-h., or an average of 1.68 kw.-h. for each of ten softening point determinations.

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[1] It is recommended that a 10–12 kw. transformer be used. The transformer and ratio board may be purchased for approximately $250.

Several rates of heating have been tried and the most satisfactory results were obtained by increasing the temperature by about 400°C per hour for three hours, which insures uniform temperature throughout the hot zone. From this point it is very easy to increase the temperature according to the requirements specified for this test by the A. S. T. M. The maximum temperature reached in this furnace was 1830°C, but the magnesite rings deteriorate rapidly above 1750°C.

The length of service of the furnace will, like all other furnaces, depend upon the treatment it must undergo. The magnesite muffle will be the first part that must be replaced, but this operation, as will be noted from the drawing, is a simple one. The carborundum ring can be used successfully for about ten heats and its replacement is also easily accomplished. The other parts of the furnace are affected very little and their replacement cost is practically negligible.

Results

The data shown in the following tables are representative of results obtained in the determinations of softening points of various materials.

The temperatures shown in Table I are the results of several check tests and are believed to be accurate within 25°C. They agree as well as can be expected with the values obtained by Kanolt[1] and are in accidental agreement with the results obtained by Hoffman[2] determined in the Reichsanstalt on German cones. We could reasonably account for even a greater difference between our values and those given by Hoffman con-

TABLE I.

The temperatures obtained by using the furnace described are those readings of an optical pyrometer when sighting directly on orton pyrometric cone. The rate of heating was that specified in the A. S. T. M. standard method of test for softening points, serial designation C24–20, and the temperatures given are those noted when the tip of the cone touched the plaque

	Temperature in °C		
Cone number	Kanolt's Orton's	Hoffman's Seger's	Author's Orton's
26	1600	1580	1550
27	1630	1605	....
28	1635	1610	1590
29	1650	1625	1605
30	1670	1640	1630
31	1670	1640	1650
32	1705	1670	1670
33	1720	1680	1690

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[1] Bur. Stand., *Tech. Paper* **7**, p. 15.

[2] *Tonind. Zeit.*, **33**, 1577 to 1580 (1909).

sidering the difference in temperature scale of the two national laboratories and the difference in the cones themselves.

The data shown in Table II compare the results obtained in the electric furnace described and a gas-fired furnace of the surface combustion type.

In Table III we have compared results obtained in our furnace with those obtained in an Arsem furnace (a graphite resistance, vacuum furnace).

TABLE II

Some results which were obtained in a gas-fired furnace of the surface combustion type formerly used at the bureau compared with those obtained in the electric furnace described. The results are shown in cones only since even fairly accurate temperature measurements are difficult to obtain in a gas-fired furnace

Material	Sample number	Softening point (cone number) as determined in gas-fired furnace			Softening point (cone number) as determined in electric furnace		
		(1)	(2)	(3)	(1)	(2)	(3)
Mo. Fire Brick	1	30	30	32	32+	32+	32+
Mo. Fire Brick	2	33	33+	..	33+	33+	..
Mo. Fire Brick	3	32–33	32–33	32–33	32–33	32–33	..
Pa. Fire Brick	1	34	34+	..	33—	33—	33—
Pa. Fire Brick	2	28	28	..	28+	28+	..
N. J. Fire Brick	1	30	31	31	30	30	30
N. J. Fire Brick	2	30	30–31	31	30	30	30
N. J. Fire Brick	3	32–33	32–33	..	32–33	32–33	..

TABLE III

Relation of softening points as determined respectively in an Arsem furnace and in furnace described

Test specimen, fire brick	Arsem furnace, degrees C	Author's furnace	
		Degrees C	Cone
A	1620	1605	28+
B	1625	1610	29
C	1645	1640	30+
D	1670	1660	31–32
E	1680	1680	32+

In the Arsem furnace the samples were protected from the reducing gases of the graphite heater by a sillimanite tube. Being heated in a vacuum there could be no oxidation. The rate of heating was 10°C per minute and the softening point was taken as the temperature at which the sample was distinctly seen to flow. This method is one which has been used in the Pyrometry Section of the Bureau, where temperature measurements are standardized and where our optical pyrometer was calibrated. One may use this comparison with due attention to the fact that small differences should be expected since different methods were used in obtaining softening point.

The softening points of various commercial grades of silica were all found to be about 1690°C which is in fair agreement with results obtained by Kanolt[1] on the melting point of silica brick.

Remarks

The advantages of this type of electric furnace are: the high temperatures obtainable, oxidizing atmosphere in the muffle, ease of control and repair, economy in operation, sufficient accuracy in determining softening points in terms of standard cones or actual temperature readings, greater convenience due to the elimination of the noise of gas burners, the fact that the operator can make observations and replace test sets without danger of burns, and the compactness of the installations.

The author wishes to acknowledge his appreciation for the constructive suggestions and criticisms offered by R. F. Geller, during the development of this furnace.

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[1] Bur. Stand., *Tech. Paper* **10,** p. 16.

RUBBER GRINDING MILL LININGS AND RUBBER AS A MATERIAL TO RESIST ABRASION[1]

By B. W. Rogers

ABSTRACT

For the benefit of those who are skeptical about the ability of rubber to resist abrasion, attention is called to the fact that a rubber tire wears much less than skid chains on a brick pavement. Rubber linings in ball mills are found more efficient than steel linings in respect to capacity, fineness of grind, and power consumption. One test on cement using both a rubber and a steel lined mill showed a 20% greater capacity, 10% less power consumption and 0.9% more material through 200-mesh. Other advantages of rubber linings are: weight of mill decrease and volume increase, reduction of maintenance costs, minimum contamination of materials being ground, and possibility of jointless and detachable linings.

It has been the popular theory that it took a very hard surface to resist abrasion successfully. This accounts for the selection of imported silex and alloy steels for the lining of grinding mills. Every grinding mill operator knows the excessive cost and delay which are incident to the replacement of worn liners and it was with this thought in mind that the idea was conceived to make the grinding mill liners of rubber. No doubt the suggestion came from the remarkable service rendered by the rubber tread on the automobile tire and to those who are unfamiliar with that peculiar property of rubber to resist abrasion, the example of the tire tread and the skid chain will visualize a basis of comparison.

Everyone who has driven a motor car and has used skid chains knows that a few hours of driving on brick or concrete roads will wear the alloy steel links to a point of failure, while in the same period of time a tire tread will not show a sign of abrasive wear.

The idea of using rubber as a grinding mill lining originated in Canada and was first made use of in the mining industry. The early experiments proved highly successful and it has been conclusively demonstrated that rubber lining can, under average conditions, commercially compete with stone, iron or steel lining on a cost and service basis.

Capacity and Efficiency

When the rubber lining was introduced, one of the first questions asked was regarding the capacity and efficiency. Rubber being a soft material, it is quite natural to assume that a certain amount of grinding is eliminated by the grinding media contacting on the soft surface. It was observed that mills with rubber linings had a higher grinding efficiency than when the same mills were lined with steel. The term "grinding efficiency" in this instance takes into consideration the three important factors (1) capacity (weight of material ground per operating time); (2) fineness of finished product in relation to the feed, and (3) power consumption. Rubber lining increased the efficiency in excess of 10% as compared with the steel lining.

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[1] Presented at the Annual Meeting, American Ceramic Society, Feb., 1925, Columbus, Ohio. (Enamel Division.)

A large cement company saw the possibilities in the rubber lining for the fine grinding of cement slurry and offered their coöperation in making operating tests. Steel and rubber lined mills were operated in parallel and observations were made varying all operating conditions such as dilution of feed, speed and grinding charge. Also, lights were extended into the mill so that the action of the grinding charge could be observed and studied. After some manipulation conditions were determined where the mills under test would operate most efficiently and the figures quoted below represent the best result with No. 1 mill operating with a rubber lining in comparison with the best results obtained from No. 2 mill operating with steel lining.

	Rubber	Steel
Gallons of slurry per hr.	2090	1740
Tons reduced to dry material	9.76	8.15
KWH per ton	13.5	14.88
Fineness	94.1–200-mesh	93.2–200-mesh

An analysis of the figures just quoted will show a 20% greater capacity for the rubber-lined mill with about 10% decreased power consumption and at the same time an increase in fineness of finished product by 0.9% through 200-mesh.

All of the experimental work to date has been accomplished in mills of the continuous feed and discharge type. There is no evident reason why the lining will not give about the same performance in the batch type pebble mill commonly used in the ceramic industry.

It was found that slippage between the shell liner and grinding media is detrimental to a violent action of the balls or pebbles. When slippage is eliminated or reduced to a minimum, the grinding media travels in a well-defined path giving a maximum of moving contact within the grinding media itself.

In replacing a stone liner with rubber the volume of the mill will be increased. Also a substantial weight will be taken off of the trunnions to allow for the possible increase in weight of the effective charge.

Probably the outstanding justification for the rubber lining is its exceptional wearing ability which will allow continuous operation over a long period of time and substantially reduce maintenance cost.

In enamel grinding rubber will conform to another important requirement, namely, the elimination of contamination. After the first few hours of operation contamination from the rubber is negligible and the smooth, impervious surface of the rubber lining can be quickly washed clean when change of grade or color is required.

A Jointless Lining

The Goodrich Company has perfected an integral bonding of soft abrasion resisting rubber. This will eliminate joints and make a leak-proof lining. This process involves a special preparation of the metal parts, therefore, it will be necessary to send such parts to the factory for the placement of the liner. This is recommended for all mills under three feet diameter. The mill will have a detachable head as it is impossible to work through small manholes.

A Detachable Lining

The rubber can be furnished in sheet form with or without fabric back and can be secured by rubber covered retaining bars. There is also the possibility of making a false lining of sheet metal to which the rubber can be applied at the factory.

For straight cylindrical type mills larger than three feet diameter, a removable wave type liner has been designed which incorporates a totally covered steel retaining bar by means of which a positive anchorage is made with bolts. The slabs are of such size that they can conveniently be entered through a standard manhole.

The experiments to date with the wave type lining show that it practically eliminates slippage of the grinding media and creates an ideal action within the mill.

The compounding laboratories have produced a new compound which will be known commercially as "Linerite." This rubber compound is without question the best abrasion resisting test on the market today and offers possibilities of application wherever a protective coating to resist corrosion and abrasion is required. It is being used successfully in mining plants, cement plants and stone washers and is particularly desirable when mounted on sheet or plate metal, giving the qualities of a rubber surface combined with the strength of steel. This new product can be worked much the same as sheet metal, its only limitation being that it cannot endure heat in excess of 150°F.

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ORIGINAL PAPERS

THE ELECTROLYSIS OF SODA-LIME GLASS—PART II[1,2]

By J. W. Rebbeck, M. J. Mulligan and J. B. Ferguson

ABSTRACT

The electrical resistance of soda-lime glass is markedly increased by suitable heat treatments. An investigation has been carried out upon the effect of the time of annealing on the resistance and the temperature coefficients of the resistances of annealed and unannealed glass. Migration experiments indicate that the major factor in the increasing of the resistance by annealing is probably a decrease in the speed of the carriers. The apparent resistance of glass is also a function of the extent to which the glass has been electrolyzed. In unaltered glass the conduction is in accord with Ohm's Law but with glass that has been electrolyzed under certain conditions the apparent resistance is a function of the applied voltage.

Studies in Electrical Resistance

Tool and Eichlin[3] have recently shown that both the density and the thermal behavior of glass may be altered by proper heat treatments and intimate that perhaps other properties may also be affected by such treatments. In line with these deductions are the observations of many other investigators. Foussereau[4] was perhaps the first to note the marked

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[1] Contribution from the Chemistry Department, University of Toronto.

[2] Part I—"Evolution of Gas and Its Relation to Sorption and Conductivity," J. W. Rebbeck and J. B. Ferguson, *Jour. Amer. Chem. Soc.*, **46**, 1991 (1924).

[3] Tool and Eichlin, *Jour. Amer. Ceram. Soc.*, **8**, 1 (1925); *Jour. Op. Soc. Am.*, **8**, 419 (1924).

[4] Foussereau, *Compt. rend.*, **96**, 785 (1883).

effect of annealing upon the electrical resistance and was followed by Gray and Dobbie[1] who carried out a partial investigation of this phenomenon in 1900. The present paper deals with certain aspects of this problem and with an allied problem—the changes in the electrical resistance induced by electrical treatments.

General Procedure

The measurements were made with glass tubes similar to those described in Part I. The tubes were constructed from tubing 11 mm. bore and 0.7 mm. wall thickness, and tubing 4 mm. bore and 0.7 mm. wall thickness. The thicker part of each tube was 6–8 cm. long and the other part was of sufficient length to eliminate errors from electrical leakage. The soda-lime glass was similar to that used in Part I.[2] The tubes were partly filled with mercury by distillation in a good vacuum. The resistances were determined by measuring with a potentiometer the fall of potential across a standard resistance which was in series with the sample tube. The form of the sample tube and the scheme of the electrical connections are given in Fig. 1. The outer electrode, in all the experiments conducted below 100°C, was an aqueous solution of sodium hydroxide of approximately 5% by weight. At higher temperatures either glycerine or molten silver nitrate was used. Constant temperatures were obtained by means of controlled water or air baths. Electrical leakage was observed by withdrawing the wire connecting the inner electrode to a position just above the surface of the mercury and taking a reading with the potentiometer.

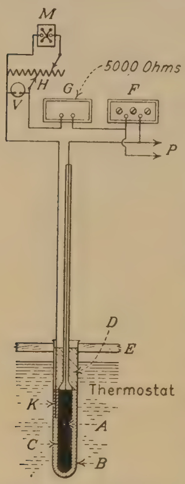

Fig. 1.—Apparatus for resistance measurements.

Ohm's Law

When the time of measurement did not exceed a few seconds, the resistance measurements with unaltered glass[3] were independent of the direction of the current. Both at 75°C and 94°C we were unable to detect deviations from Ohm's Law with unaltered glass greater than our experimental errors (one per cent or less) though we used potential gradients ranging from 322 to 1610 volts per cm. A few results at 46 and 60°C indicated a similar behavior at these lower temperatures. The experiments were carried out with both ordinary and annealed glasses[1] and agree with those made at higher temperatures by a number of investigators,[2] who found that this law held for similar glasses in the temperature interval 191–350°C. The fact that Ohm's law is obeyed at the lower temperatures noted by us would seem to render probable the assumption that the law also holds at room temperature for the kinds of glass and the range of potential gradients used by us at the higher temperatures.

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[1] Gray and Dobbie, *Proc. Roy. Soc.* (*London*), **67**, 200 (1900).

[2] SiO_2 71.08%, Na_2O 18.85%, CaO 6.22%, MgO 3.38%, with small amounts of Al_2O_3, Fe_2O_3, ZnO.

[3] By unaltered glass we mean glass, the composition of which has not been changed by electrolysis.

Annealing

The effect of annealing upon the resistance was first noted by Foussereau and later studied by Gray and Dobbie. The relation between the time of annealing and the electrical resistance was investigated by us in the following manner. A number of tubes were constructed from a length of large and a length of small tubing and then placed in the electric furnace at 400°C. The tubes were withdrawn from the furnace singly after different intervals of time and when all had been removed were filled with mercury by distillation, placed in the water bath at 74.3°C and the resistance of each determined. The results of these measurements together with the results obtained with other tubes annealed for 1600 hours are given in Fig. 2. Certain measurements at 94.1°C indicated that a similar curve would have been obtained had these resistance measurements been carried out at that temperature.

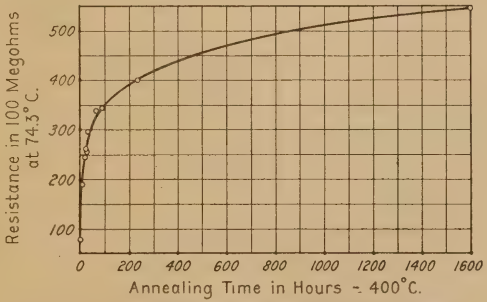

FIG. 2.—The relation between time of annealing and the electrical resistance.

The permanent nature of the change in the resistance which may be brought about by annealing was previously noted by Gray and Dobbie and we were able to confirm their observations. Thus resistance measurements on May 21, 1923 with tubes No. 84, No. 85, and No. 87, yielded for the specific resistances respectively 43.3, 42.9 and 38.9 × 10^8 ohms. Similar experiments on tube No. 88 of the same series gave on Dec. 19, 1923 a value of 40.7 × 10^8 ohms. The slight differences here shown are due to experimental errors such as errors in the determination of the true dimensions of the glass.

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[1] In this paper we are using the word annealed to designate a heat treatment at high temperatures. Usually we heated the tubes exposed to the atmosphere in an electric furnace at 400°C for many hours. The temperature varied slightly with changes in the line voltage.

[2] Warburg, *Wied. Ann.*, **21**, 622 (1884); Tegetmeier, *ibid.*, **41**, 19 (1890); LeBlanc and Kerschbaum, *Z. physik. Chem.*, **72**, 468 (1910); Schulze, *Ann. Physik*, **37**, 435 (1912).

Temperature Coefficients The change in the resistance of the glass upon annealing was so marked that it seemed advisable to determine if the temperature coefficients of the resistance were similar in the two cases. For this purpose tubes were annealed by heating for 24 hours at 400°C. The results are given in Fig. 3; the values for the unannealed glass agree with those published by Holladay.[1] The change in the slope of the curve due to annealing, *i. e.*, the change in the temperature coefficient, might have been caused by a slight change in composition judging from Holladay's results. The resistance-temperature function does not change in form but only in the value of the constants.

A few measurements were made with a lead glass (PbO 52.9%) and these results are included in the diagram.

Migration Experiments The purely electrical resistance measurements do not afford any positive clue as to the nature of the change which is induced in the glass by a proper heat treatment. A method of attack upon this phase of the problem may be based upon the electrical migration of silver into glass.

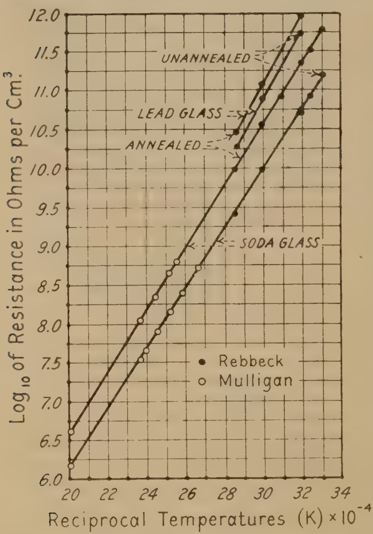

FIG. 3.—The relation between temperature and electrical resistance.

Schulze[2] has studied both the thermal diffusion and the electrical migration of silver into glass. He found that in the thermal diffusion the silver in the silver nitrate melt replaced the sodium in the glass and that both thermal diffusion and electrical migration took place at the same time. He also noted that some diffusion took place when the direction of the current was reversed. The diffusion phenomenon is, therefore, one that must be considered in connection with migration experiments. Provided that the diffusion phenomenon does not mask the migration effects, it should be possible by migration experiments to check our resistance measurements on annealed and unannealed glasses and to obtain some idea of the carriers of the current in these glasses. For this purpose are required the weights of the silver electrolyzed into the glass and the thicknesses of the layers produced. The weight of the silver may be obtained if we know (1) the total increase in weight of the glass in the experiment, (2) the thermal diffusion blank. The weight increase may be directly observed by weighing the cleaned tube before and after the experiment. The thermal diffusion blank consists of two blanks: the blank due to thermal diffusion before and after electrolysis, and the blank during electrolysis. The former blank may be obtained from tubes immersed in the melt simultaneously with the tube under investigation. The latter blank can only be obtained by difference from the actual weights obtained and the weight calculated from the current measurements. The thickness of the silver layer may be easily determined with a microscope, since upon heating the glass containing the silver the layer becomes brownish in color and the boundary is quite sharply defined.

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[1] Holladay, *Jour. Franklin Institute*, **195,** 229 (1923).

[2] Schulze, *Ann. Physik*, **40,** 335 (1913).

The details of a typical experiment are as follows: Two annealed and two unannealed tubes were cleaned by the method used by Schulze[1] and weighed. They were then filled with mercury by distillation in a good vacuum and placed in a bath of molten silver nitrate. One tube of each kind was then electrolyzed with mercury cathode at constant voltage. The duration of each stage of the process was noted and the current flowing observed with a precision potentiometer as in the resistance measurements.

TABLE I

	Total time 185 minutes. Applied e.m.f. 108 volts			
Temperature 223–231 °C. Time of electrolysis 142 mins.	Tube No. 307D unannealed electrolyzed		Tube No. 309A annealed electrolyzed	Tube No. 305D unannealed not electrolyzed
Wt. silver in glass	0.0809 g.		0.0313 g.	0.0108 g.
Thermal diffusion blank before and after electrolysis	0.0023		0.0013[2]	
Total silver less T. D. blanks		0.1086		
Total silver for current		0.1052		
Probable T. D. blank during electrolysis	0.0022		0.0012	
Layer thickness	8.9%		4.6%	
Ratio silver electrolyzed into the tubes (unannealed to annealed)		$\frac{2.66}{1}$		
Ratio glass conductivities from current measurements		$\frac{2.77}{1}$		
Ratio conductivities from previous resistance measurements		$\frac{2.75}{1}$		
Ratio thickness of layers		$\frac{1.9}{1}$	(thermal diffusion neglected)	

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[1] Schulze, *Ann. Physik,* **37,** 438 (1912).

[2] This value assumed from other experiments.

At the close of the electrolysis, the tubes were removed, cleaned and weighed. They were then heated in the flame of a Bunsen burner to bring out the color and the layers observed under the microscope. Experimental difficulties prevented the completion of any whole set of measurements, but from a number of partially completed series we were able to check the one nearly complete series given in Table I.

These results confirm our previous work which indicated a marked increase of resistance upon annealing. They provide no evidence in favor of the theory that sorbed gases and vapors are engaged in the conduction process.[1]

If the change in resistance induced by annealing arose from a decrease in the speed of the ions alone, the ratio of the thicknesses of the layers would have been equal to the ratio of the conductances. On the other hand, if the change were due to a decrease in the number of carriers, *i. e.*, a decreased ionization, then the layers would have been of equal thickness, but of different densities. The theory that the change is due to a decreased ionization is perhaps the logical one for a chemist to propose and has been tentatively suggested by Sutton and Silverman;[2] however, in the experiments quoted and in many others, the layer thicknesses were in the ratio of approximately 2/1, whereas the conductances were in the ratio of nearly 3/1. These facts lead us to believe that the major factor in the change must be a decrease in the speed of the ions, but that there is also a slight change in the number of carriers as well.

Remarks on Annealing

The resistance of the glass does not appear to be affected in any reasonable time at temperatures below 100°C, but at temperatures above 300°C allowance must certainly be made for changes due to annealing. Thus the estimates made by Schulze concerning the resistance of glass containing silver and the deduction of Kraus and Darby[3] relative to the ionization of glass at different temperatures may be affected by this source of error.

Electrical Treatment

The true resistance of a piece of glass is obtained with direct current when the glass remains unaltered in composition during the time of the measurements. The ideal way to ensure that this will be the case would be to choose such electrodes that the same ions migrate into the glass on the one side as are migrating out of the glass on the other side during the time of measurement.

Even if the conditions just outlined cannot be fulfilled the time of measurement may be so shortened that errors due to electrolysis may become negligible and the values obtained be independent of the direction of the current.

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[1] See Part I for further discussion of this point.

[2] Sutton and Silverman, *Jour. Amer. Ceram. Soc.*, **7,** 86 (1924).

[3] Kraus and Darby, *Jour. Amer. Chem. Soc.*, **44,** 2783 (1922).

When the electrolysis has proceeded for some time, this latter statement does not hold and with a set-up in which the electrodes differ in character, such as the one used by us, the measured resistances are very dependent upon the direction of the current.

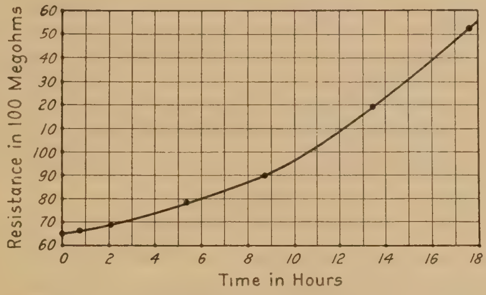

FIG. 4.—The change in the electrical resistance due to continued electrolysis with mercury anode.

When the current flows from the sodium hydroxide solution (mercury cathode) the apparent resistance changes but little during an extended electrolysis. Even after many hours, the total increase does not amount to more than a few per cent and small counter electromotive forces may be observed if the source of potential be removed from the circuit and the latter closed. These polarization voltages quickly fall to values which remain nearly constant for many hours. The latter values are dependent in magnitude upon the time of electrolysis and range from one to two volts. The glass in this case behaves somewhat as a storage battery. Brace[1] has recorded that he has observed similar effects with porcelain.

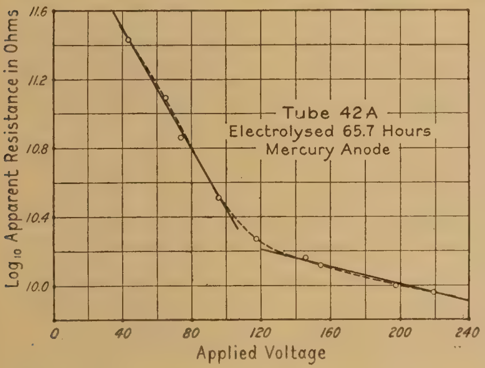

FIG. 5.—The relation between the apparent resistance and the applied voltage.

When the current flows in the reverse direction (mercury anode) the apparent resistance increases continuously as the electrolysis proceeds. In Fig. 4, the results of an experiment[2] at constant applied voltage with unannealed glass are given. These results were confirmed by two other independent experiments. The curve shows that, although the quantity of current passing through the glass in a unit of time becomes less as the electrolysis proceeds, the rate of change of the resistance with time appears to increase. The apparent resistance of a tube which has been electrolyzed for a long time with mercury anode is, however, a function of the applied voltage. The relation existing between the apparent resistance and the applied voltage for one tube[1] is shown in Fig. 5, in which the logarithm of the resistance is plotted against the applied voltage. The apparent resistance decreases as the voltage rises and for certain ranges of applied voltages, this apparent resistance is approximately an exponential function of the applied voltage. Now Poole[2] has found that at high voltages glass does not conduct electricity according to Ohm's law but that the logarithm of the resistance is nearly a linear function of the applied voltage. The gap between his experimental conditions and our own is perhaps too great to warrant an extrapolation but our results suggest that he may not have been dealing with unaltered glass.

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[1] Brace, *Trans. Amer. Electrochem. Soc.*, **33**, 205 (1918).

[2] The electrolysis was carried out at 74.3° with 110 volts.

Two explanations have been given for the change in resistance upon electrolysis just described. Schiller[3] tentatively suggests that there is a polarization phenomenon which is a function of the applied voltage, while the work of Warburg, LeBlanc and Kerschbaum, and Schulze[4] at higher temperatures seems to indicate that high resistant layers are the major factor. LeBlanc and Kershbaum were able to prepare glasses in which the conduction process was no longer ionic in character and in which the current was proportional to the square of the applied voltage.

We have a great many observations upon this phase of the subject and many of our results indicate that the behavior of glass under such conditions may be similar to that of some other dielectrics. The nature of the so-called absorption currents and residual currents is in fact the point in question. The present status of our work does not permit us to discuss this point at length, but we have many experiments which do not seem to be explained by the high resistant layer theory and which point fairly conclusively to a type of polarization phenomenon as an ultimate explanation.

Summary

1. The relation between the thermal history and the electrical resistance of glass has been investigated. Curves are shown which indicate (1) the change of resistance with time of annealing and (2) the temperature coefficient of the resistances of annealed and unannealed glasses. From electrical migration experiments, using silver nitrate, the marked increase in the resistance which may be produced by annealing appears to be due more to a change in the mobility of the sodium ions than to a decrease in the number of these carriers.

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[1] The tube was previously electrolyzed with 100 volts at 94.1°.

[2] Poole, *Phil. Mag.*, **42,** 501 (1921).

[3] Schiller, *Ann. Physik,* **74,** 105 (1924).

[4] Warburg, *loc. cit.;* LeBlanc and Kerschbaum, *loc. cit.;* Schulze, *Ann. Physik,* **37,** 435 (1912).

2. The apparent resistance of a glass sample may or may not increase markedly upon prolonged electrolysis depending upon electrode conditions. In the cases in which we observed great increases, the apparent resistance is a function of the applied voltage. Our results at 75° and 94°C tend to support the polarization theory of such increases at low temperatures rather than that based upon high resistant layers, but are as yet too few for a definite conclusion.

Acknowledgment

Mr. Mulligan is at present the holder of one of the Bursaries granted by the Research Council of Canada and we wish in conclusion to express our appreciation of their assistance which has materially aided in the prosecution of this work.

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ANALYSIS OF RECENT MEASUREMENTS OF THE VISCOSITY OF GLASSES

By Gordon S. Fulcher[1]

ABSTRACT

Viscosity of Simple Soda-Silicate Glasses, 500° to 1400°C

Comparison of the results given by English with those of Washburn, Shelton and Libman, indicates a discrepancy in the absolute values of $\log_{10}$ viscosity amounting to 0.6, those of Washburn *et al.*, being relatively too high. If correction for this is made, the isothermal curves of $\log_{10}$ viscosity as a function of soda content are smooth up to 50% Na_2O, showing no inflection. The observations as a function of temperature T are all represented within accidental error by an equation of the type

$$\log_{10} \eta = -A + B \times 10^3 / (T - T_0)$$

where all three constants vary regularly with the composition.

Change of Viscosity of Glass ($6SiO_2$, $2Na_2O$) due to Molecular Substitution of CaO, MgO and Al_2O_3 for Na_2O

The effect is clearly brought out by plotting (from the results of English) the change of $\log_{10} \eta$ due to the substitution as a function of temperature. The curves each show a sharp bend at a temperature between 840° and 1050°C, which is designated the aggregation temperature T_a. If we divide these curves by the corresponding percentage substituted, we get curves for each oxide which are straight and parallel below the aggregation temperatures, the slopes (increase of change of $\log_{10} \eta$ per 100°C) being -0.056 (CaO), -0.055 (MgO), -0.018 (Al_2O_3) per per cent oxide substituted. For substitution of $^1/_2$ molecule the slopes are -0.325 (CaO), -0.23 (MgO) and -0.18 (Al_2O_3) per 100°. At the aggregation temperature the change of $\log_{10} \eta$ per per cent is a minimum, 0.03 to 0.06 for CaO, 0.12 for MgO, 0.07 for Al_2O_3.

Evidence of Aggregation in Glasses, from Viscosity Measurements

The sharp bends in the plots of change of $\log_{10} \eta$ due to substitution of an oxide for Na_2O, suggest the beginning of molecular aggregation at these temperatures. These aggregation temperatures are close to the devitrification temperatures, but the effect on the viscosity curves cannot be due to actual devitrification since it does not change with time. Taking the aggregation temperatures as equal to devitrification temperatures, additional isotherms are roughly sketched into the *equilibrium triangle of the system* Na_2O–CaO–SiO_2.

Change of Viscosity of Glass ($4SiO_2$, $2Na_2O$) due to Substitution of B_2O_3 for SiO_2

The change of $\log_{10} \eta$ (from the results of English) is plotted as a function of temperature, and also the change of $\log_{10} \eta$ per per cent B_2O_3. The curves are more complex than for the substitution for Na_2O.

Introduction

To the glassmaker the viscosity of his glass, particularly at the higher temperatures, is of the greatest importance. The refining of glass depends on the rate at which the gas bubbles rise and this varies with the viscosity; the weight of the gather, the size of the gob fed through an orifice, the distribution obtained in a blown article, the sharpness with which the glass takes the form of the mold, and the rate of annealing, each depend upon the viscosity of the glass through the corresponding range of temperature. Nevertheless until recently no accurate measurements have been made. During the past year, however, the results of two extensive, systematic and carefully made investigations have been published. S. English[1] studied the viscosity of several series of soda-lime, soda-magnesia and soda-boric oxide glasses at temperatures from 500° to 1400°C. Just previously Washburn, Shelton and Libman[2] obtained values for a series of soda-lime glasses for the range 800° to 1500°C. It seemed worth while to subject the data to a graphical analysis in order to correlate and compare the results of the two investigations and to get as much information as possible from them as to the variation of viscosity with temperature and with composition.

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[1] Recd. March 20, 1925.

The method of measurement used in the two investigations is the same in principle. In both cases the glass was melted to a definite depth in a porcelain crucible held at the desired temperature by means of an electric resistance furnace, and the viscosity was measured by the rate at which a given torque, applied by means of a weight hung on a silk thread, rotated a rod mounted on ball bearings which carried a stirrer which was carefully centered and immersed to a definite depth in the glass. The furnaces were somewhat different, that of English having been relatively quite long while that of Washburn *et al.*, closely fitted the crucible and was supplied with independent heating wires in the lid as well as on the sides and bottom and was controlled by means of three thermocouples, while English used only one. The stirrer used by English was cylindrical and covered with an iridio-platinum sheath, while Washburn *et al.* used a carefully formed porcelain stirrer with a relatively small neck where it passed through the surface of the glass. Both pieces of apparatus appear to have been carefully calibrated and the precision obtained in each case seems to be about the same. A careful reading of both articles did not suggest any definite reason why the results obtained in the two investigations should not be given equal weight.

For temperatures from 500° to 750°C, it is impossible to use the above method, so English obtained values for the viscosity from measurements of the rate of elongation of a rod or thread under a given applied load.

In the following analysis, the various glasses will be designated by the authors' numbers, followed by an E or a W, to indicate English or Washburn *et al.*

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[1] S. English, *J. Soc. Glass Tech. Trans.*, **7,** 25 (1923) and **8,** 205 (September, 1924).

[2] E. W. Washburn, G. R. Shelton and E. E. Libman, Univ. of Illinois Eng. Exp. Station, *Bull.* **140,** 74 pp. (April, 1924).

1. Sodium Silicate Glasses

Results are given for the following glasses:

Glass	Na_2O, per cent	R_2O_3, per cent	RO, per cent	Loss ($H_2O + CO_2$), per cent	Ratio of Na_2O to SiO_2
2W	17.0	0.46	0.0	0.8	0.207 = 1/4.84
600E	19.46	.80	.1	?	.244 = 1/4.1
1E	25.34	.42	.2	?	.342 = 1/2.93
3W	29.5	1 (about)	.1	?	.43 = 1/2.32
4W	39.3	1 (about)	.1	?	.67 = 1/1.5
1W	49.4	0.6 to 1.8	.1	2.5	1.03 = 1/0.97

The data for 1E extend from 485° to 1310°C. When log η (η = viscosity) is plotted as a function of temperature (see English, Fig. 6)

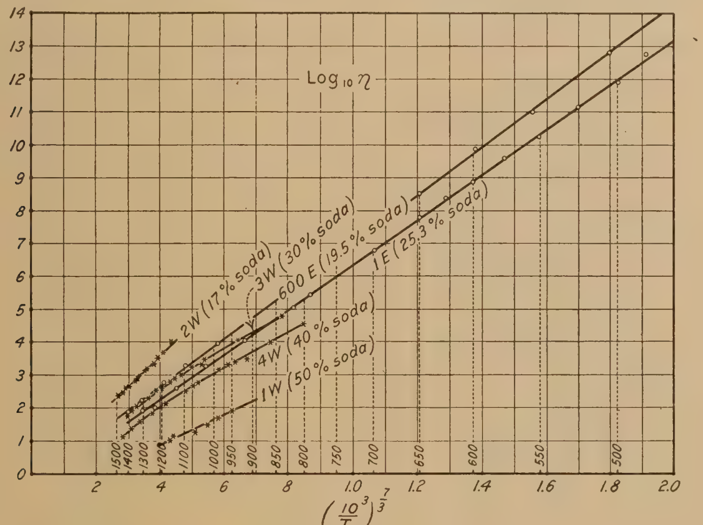

FIG. 1.—Observed values of $\log_{10} \eta$ as a function of $(10^3/T)^{7/3}$. Smooth curves drawn through experimental points.

a curve concave upward is obtained, log η decreasing less rapidly the higher the temperature. Let us change the variables so as to get as near a straight line plot as possible. If log η is plotted as a function of $1/T$, where T is absolute temperature centigrade, a curve concave upward is still obtained. The concavity is less if $1/T^2$ is used, and it was found that log η plotted as a function of $(1/T)^{7/3}$ gave practically straight lines both for 600E and 1E (see Fig. 1).[1] Therefore

$$\log \eta = -a + b\,(10^3/T)^{7/3}. \qquad (1)$$

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[1] Slightly better agreement with a linear relation is obtained if we assume that there is a jog of 0.17 between the line through the points below 700° obtained by the elongation method, and the line through the points above 700°. If we subtract 0.17 from the values for the lower temperature the data for 1E are represented within experimental error (±0.03) by the equation (1E) $\log_{10} \eta = -0.40 + 6.66(10^3/T)^{7/3}$.

In Fig. 1 the results for glasses 1W, 2W, 3W or 4W have also been plotted and full lines have been drawn through the observations so as to represent them as closely as possible. The curves for 3W and 4W are definitely concave downward. But the most interesting fact brought out in this figure is the marked discrepancy between the E and W curves, not so much in the shape as in the absolute values. The 3W curve for 30% soda crosses the 1E curve (25.3% soda) at 850° and nearly touches the 600E curve (19.5% soda) at 1400°, while the 2W curve (17% soda) is farther above the 600E curve (19.5% soda) than the 4W curve (40% soda) is below it. If the results for a certain temperature, say 1200°, are plotted as a function of the ratio of soda to silica *r*, an irregular curve is obtained, as shown in Fig. 2*A* by the dotted line *abcde.*

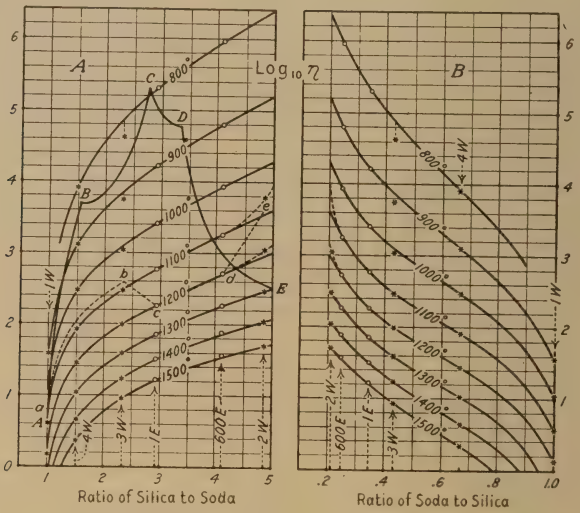

FIG. 2.—Value of log$_{10}$ η as a function of composition for various temperatures.

Now it is possible, of course, that this dotted curve represents the real relation between viscosity and composition. The only other evidence we have is by Morey and Bowen[1] who recently determined the equilibrium diagram for soda and silica. The devitrification curve given by them shows corners at compositions 23, 26.5 and 39.2 per cent soda corresponding to ratios $r = 3.34$, 2.77 and 1.55. On Fig. 2 the curve *ABCDE* shows log η at the devitrification temperature as a function of *r*.

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[1] Morey and Bowen, *J. Phys. Chem.*, **28**, 1174 (November, 1924). The devitrification temperatures plotted in Fig. 2 are as follows:

r =	0.97	1.55	1.94	2.77	3.03	3.34	4.85
T_d =	1088°	840°	874°	793°	842°	870°	1280°

There is no relation evident between curves *abcde* and *ABCDE*, and we must conclude that the viscosities of the sodium silicates are not influenced by any tendency to devitrification. Therefore until measurements on more compositions have been made we must assume that the curve showing the relation between log η and r is a smooth one.

Returning to curve *abcde*, it is evident that the two E values are relatively too low to fit in with the W values. It was found that when 0.6 is subtracted from each of the latter, all the values lie on the smooth curves shown of the full lines in Fig. 2, except the values for 2W for 1200° and below, which seem too high, indicating devitrification, and the values for 3W for 1000° and below which seem too low.

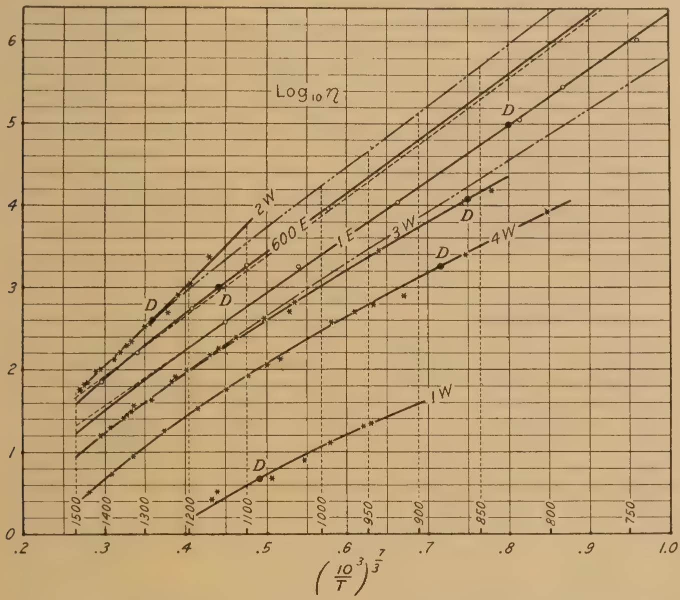

FIG. 3.—Values of $\log_{10} \eta$ as a function $(10^3/T)^{7/3}$ with values for W curves decreased by 0.60.

Figure 3 shows the same curves as Fig. 1, for temperatures above 750°, with the W curves displaced downward 0.6. The curves drawn with lines and dashes represent the smoothed values from Fig. 2 where these differ from the full line values. The dotted lines represent the straight lines as drawn in Fig. 1 for 600E and 1E.

It is of interest to note that the viscosity curves for both E and W glasses extend to temperatures below that at which they should begin to devitrify, without showing any bending, except 2W. (The devitrification parts are marked by *D* on Fig. 3.)

From the curves in Figs. 2 and 3, the relative values of the viscosity of any two sodium silicates between 800° and 1500° and for r between 1 and 5 may be determined as accurately as the values upon which these curves are based, are known. But even if our curves give the relative values correctly, the absolute values are still uncertain because of the apparent discrepancy of 0.60 between the results of the two investigations. Since 0.60 is the logarithm of 4, this discrepancy means that the W viscosities are four times too large or the E values are four times too small or there are errors in both sets such that the ratio of the required correction factors is 4, for instance $^1/_2$ and 2. This conclusion emphasizes the importance of developing a reliable method of calibrating high temperature viscosity apparatus. If the absolute values for a standard glass at high temperatures were known, this glass could then be used in calibrating all such apparatus. It is suggested that future experimenters make a few runs with glasses having compositions approaching closely those of 1E, 600E and 3W so as to enable their results to be compared with those discussed in this paper.

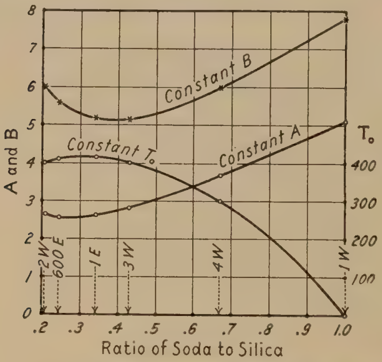

FIG. 4.—Constants in equation $\log_{10}\eta = -A + B \times 10^3/(T - T_0)$, as a function of ratio of soda to silica.

As to the mathematical representation of the curves, the data plotted in Fig. 3 indicate that the curves are not straight for temperatures above 1000° but bend downward; that is, above 100° log η varies inversely as some higher power of the temperature than $^7/_3$. Equations of the form

$$\log \eta = A - B/T + C/T^2 \tag{2}$$
$$\log \eta = -A + BT + C/T^2 \tag{3}$$
$$\log \eta = -A + B \log T + C/T^2 \tag{4}$$
$$\log \eta = -A + B/(T - T_0)^2 \tag{5}$$

may be made to represent the results more or less closely but the three constant equation which seems to fit the results best is of the form

$$\log \eta = -A + B \times 10^3/(T - T_0) \tag{6}$$

This equation with the values of the constants given in Table II fits the experimental results for both 1E and 600E (corrected by subtracting 0.17 from the values for below 750°) within the accidental errors. For the other glasses the range of temperature is too small to determine T_0 accurately so values of T_0 were chosen which give values of log η for 500°C consistent with the values for the E glasses. The constants were also adjusted so as to vary continuously with the soda-silica ratio (see Fig. 4).

TABLE II

CONSTANTS IN THE EMPIRICAL EQUATION (6) FOR SODA-SILICA GLASSES[1]

Glass	Soda/silica	A	B	T_0	Log η at 500° (calc.)
2W	0.207	2.64	6.00	400°	13.45
600E	.244	2.56	5.60	410	12.87
1E	.342	2.63	5.20	415	11.89
3W	.43	2.81	5.15	400	11.0
4W	.67	3.68	6.00	300	9.0
1W	1.03	5.08	7.80	0	5.0

In Fig. 5 are plotted the values of log η as a function of $10^3/(T-T_0)$. The observed values are indicated only for 1E, 600E and 2W; but for all the glasses the straight lines represent the smoothed values on the curves of Fig. 2 quite accurately. In the case of 2W the observed viscosity evidently increases too rapidly with decreasing temperature below 900°. This is probably due to crystallization.

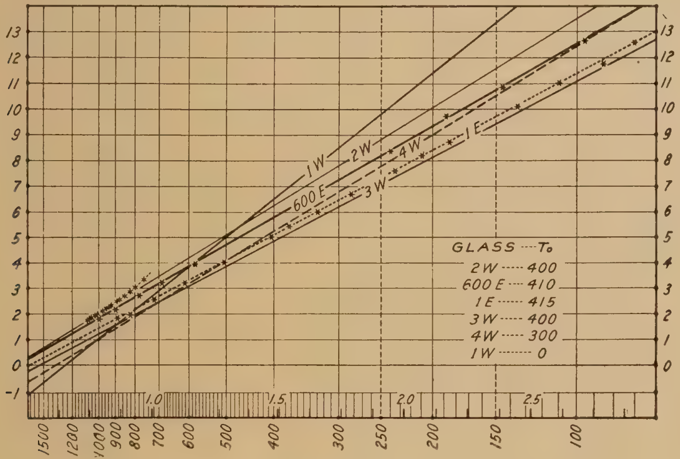

FIG. 5.—Log$_{10}$ η function of $10^3/(T - T_0)$.

Whether or not equations (1) and (6) have any physical significance, they are evidently useful for plotting in order to compare the results for different glasses or those obtained by different observers.

In two recent papers[2] LeChatelier states that when log (log η) is plotted as a function of T, two straight lines meeting at an obtuse angle are obtained for each glass. While such a plot may be convenient for interpolation purposes, it should be evident that this equation is unlike that of any of the ordinary physical equations in that the shape of the curve obtained depends not only on the base of the logarithms used (e or 10) but also on the units in which η is expressed. For instance if the values of $\log_e (\log_e \eta)$ for temperatures 1000°, 1200° and 1400° are 2.130, 1.780 and 1.430 (approximately the values for 3W) the curve is a straight line; but the values of $\log_e(\log_e e^2\eta)$ are 2.3433, 2.0707 and 1.8212, the middle value being 0.0115 less than it should be if the relation is linear, corresponding to a difference of 9.6 per cent in η. The plot of $\log_e(\log_e \eta/e^2)$ curves the other way; the middle value is greater than it should be for a linear relation, the difference of 0.191 in $\log_e \eta/e^2$ corresponding to a difference of 21% in η. Any linear relation obtained in such a plot is therefore purely accidental and can have no physical significance. The positions of the inflections reported by LeChatelier would also shift more or less with the units employed, the shift being greater the nearer the angle of inflection is to 180°. The curves plotted in Fig. 5, however, show no indications of inflection. In the case of 1E the viscosity changes in the ratio of 1 to 10^{11}, yet the results are represented within accidental error by the single straight line.

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[1] The empirical equations correspond to the observed values of log η corrected by subtracting 0.60 from all the W values and 0.17 from the E values obtained by the elongation method (below 750°).

[2] Henri LeChatelier, *Compt. rend.*, **1924**, pp. 517 and 718 (referred to in *Nature*, **114,** p. 731, November 15, 1924); *J. Soc. Glass Tech.*, **9,** 12 (March, 1925).

2. Soda-Lime-Silica Glasses

English investigated the series of glasses whose percentage compositions are given in Table III. Starting with the soda tri-silicate 1E (Na_2O, $3SiO_2$), CaO was substituted for Na_2O molecularly in steps of about 0.1 molecule up to (Na_2O, CaO, $6SiO_2$).

TABLE III

PERCENTAGE COMPOSITION OF SODA-LIME-SILICA GLASSES (ENGLISH)

Glass	CaO	Na_2O	($CaO+Na_2O$)	Equiv. Na_2O	SiO_2	Minor	Total
1E	0.21	25.34	25.55	25.57	74.05	0.38	99.98
3E	2.61	23.00	25.61	25.80	74.08	0.37	100.05
4E	3.81	21.50	25.31	25.59	74.07	0.42	99.80
5E	4.50	20.78	25.28	25.61	73.78	0.72	99.78
6E	6.26	19.38	25.64	26.00	73.18	1.40	100.22
7E	7.45	17.20	24.65	25.21	74.41	0.94	100.00
8E	8.16	16.00	24.16	24.77	74.99	0.66	99.81
9E	9.36	14.88	24.24	24.94	74.96	0.86	100.06
10E	10.38	14.22	24.60	25.37	74.59	0.96	100.15
11E	11.68	13.02	24.70	25.57	74.93	0.86	100.49

Percentage Substitution of CaO for Na_2O

Since the percentage of SiO_2 is practically constant we may consider these a series of glasses with about 74.5% SiO_2 in which CaO is substituted for Na_2O, per cent for per cent. To bring out the effect of this substitution, the *change of* $\log_{10} \eta$ *due to substitution* is plotted in Fig. 6 as a function of the temperature for each of the glasses

3E to 11E. In getting these values correction was made for the variation of percentage of ($CaO + Na_2O$) by comparing with the results for a simple soda glass having a percentage of soda equal to the percentage of ($CaO + Na_2O$) (obtained by interpolation between 1E and 600E curves). The observed changes of $\log_{10} \eta$ are indicated by points connected by dashed lines. Although these dashed curves are somewhat irregular, they each show unmistakably a sudden bend at about 900° to 1000°C. Above this temperature, the change in $\log \eta$ due to the substitution does not vary much with temperature though it shows a tendency to decrease with decreasing temperature. Below this temperature, however, the change in $\log \eta$ increases approximately linearly with decreasing temperature. The full line curves were drawn with the aid of a plot of the change of $\log_{10} \eta$ at certain fixed temperatures as a function of the per cent CaO, so that they represent the results smoothed with respect to CaO variation as well as to temperature variation.

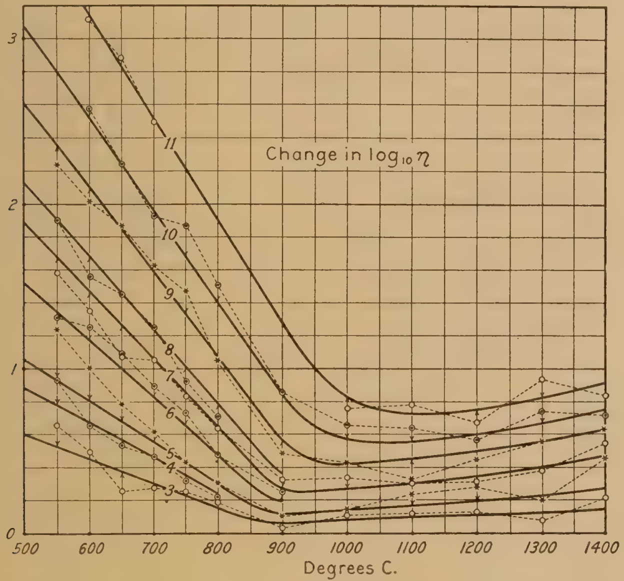

FIG. 6.—$\Delta \log_{10} \eta$ for various lime glasses as a function of temperature.

It is evident that the slopes of the low temperature parts of the curves of Fig. 6 increase with the percentage of CaO. If we divide each of the full line curves of Fig. 6 by the corresponding per cent CaO we obtain the curves of Fig. 7 which therefore give the *change in* $\log_{10} \eta$ *per per cent CaO substituted*. The low temperature parts are now parallel. While the observations are not accurate enough to prove that these curves must be exactly parallel, yet the best smooth curves drawn through the observations lead to lines which are remarkably close to being parallel.

Now as to the physical interpretation of this result. Evidently as the soda-lime glass cools, at a temperature varying from 860° (for 2% CaO) to 1010°C (for 12% CaO) some process of molecular rearrangement must start which increases the rate at which the viscosity changes with decreasing temperature. It is natural to suppose that this is a process of molecular aggregation so we shall call the temperature at which this starts the *aggregation temperature.* These temperatures will be shown to be about those at which devitrification is to be expected. Devitrification was actually observed only in the case of glasses 10E and 11E and none of the recorded points (except perhaps 750–900° for 10E) relate to devitrified glass. When visible devitrification sets in, crystals grow steadily so that consistent readings cannot be taken. The molecular aggregations responsible for the change of slope of the viscosity curves of Fig. 6 must, therefore, be sub-crystalline, for while they begin to form at a temperature at which devitrification is to be expected, yet they seem to be in equilibrium (for less than 10 per cent CaO) and to give a definite viscosity at each temperature. The fact that the curves giving change of log η per per cent CaO are parallel below 850° means that the *increase per degree of the change of log η due to the substitution of CaO is proportional to the per cent of CaO substituted;* the shift of the line to the right with increasing per cent CaO is due to the shift of the aggregation temperature to higher values.

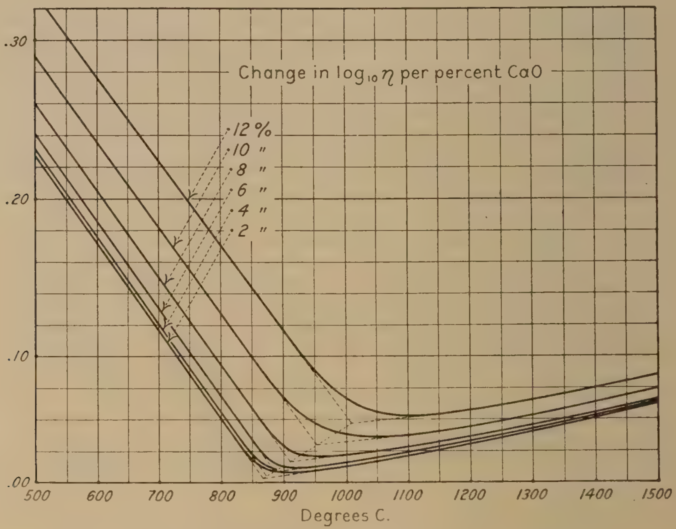

FIG. 7A —Percentage substitution of CaO for Na_2O.

Molecular Substitution of CaO for Na_2O

The curves of Fig. 7A are for substitution of CaO for Na_2O, per cent for per cent, in a sodium silicate with about 74.5% SiO_2. In case of molecular substitution, since 56 gm. of CaO are molecularly equivalent to 62 gm. of Na_2O, the silica content does not remain constant but increases slightly, in fact from 74.05 for ($6SiO_2$, $2Na_2O$) to 74.93 for ($6SiO_2$, $1Na_2O$, $1CaO$). Since increasing the silica content increases the viscosity, the changes in $\log_{10} \eta$ due to molecular substitution are somewhat greater than for percentage substitution. The smoothed results for the change of $\log_{10} \eta$ per per cent CaO for substitution of 0.2, 0.4, 0.6, 0.8 and 1 molecule of CaO in the soda-tri-silicate ($6SiO_2$, $2Na_2O$) are shown in Fig. 7B.[1]

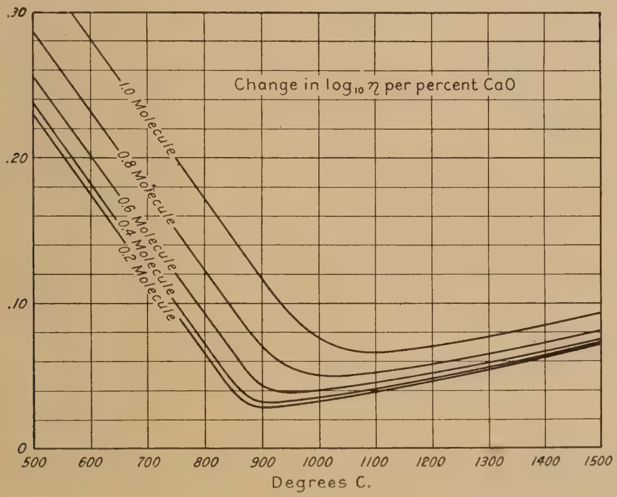

FIG. 7B.—Change in $\log_{10} \eta$ per per cent CaO, for molecular substitution of 0.2 to 1 molecule for Na_2O.

The compositions of the corresponding glasses are given in Table IV.

The variation of the aggregation temperature with per cent CaO is shown in Fig. 8, for 25% (Na_2O + CaO). The devitrification temperature for pure sodium-silicate with 25% Na_2O is about 838° according to the curve of Morey and Bowen[2] while the value for the aggregation tempera-

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[1] As shown in Table III, the equivalent Na_2O (which is the amount of soda in the simple soda-silicate in which molecular substitution of a certain percentage of CaO will give a glass of the composition of the actual glass, and therefore determines the composition of the simple soda-silicate with which the actual glass is to be compared as to viscosity) is practically constant, as was intended in making up the glasses. The slight corrections necessary were made so as to reduce all to 25.34% equivalent Na_2O. The formula for equivalent per cent Na_2O is $N' = (KC + N)/[100 + (K-1)C]$, where C is per cent Na_2O, and K is ratio of molecular weights of Na_2O to CaO.

[2] *Loc. cit.*

TABLE IV

Glass	SiO_2, per cent	Na_2O, per cent	CaO, per cent
$6SiO_2$, $2Na_2O$	74.05	25.34	0
$6SiO_2$, 1.8 Na_2O, 2CaO	74.23	22.85	2.3
$6SiO_2$, 1.6 Na_2O, 4CaO	74.40	20.4	4.61
$6SiO_2$, 1.4 Na_2O, 6CaO	74.58	17.9	6.93
$6SiO_2$, 1.2 Na_2O, 8CaO	74.75	15.4	9.26
$6SiO_2$, 1.0 Na_2O, 1CaO	74.93	12.8	11.63

ture from these viscosity measurements is 860°. The agreement is so close that one is inclined to attribute the small difference to the impurities present or to uncertainty in the determination of the aggregation temperature. The devitrification temperature of pure calcium silicate with 25% CaO is 1540° according to G. A. Rankine.[1] This point also seems to lie on the aggregation temperature curve extrapolated from 12% CaO. We may therefore conclude that the aggregate temperature given by the viscosity curve is the same as the devitrification temperature or slightly above it. However, it should be emphasized that aggregation does not seem to be the same as devitrification. It occurs promptly and reaches a limit which is a definite function of the CaO content whereas devitrification for low content of CaO, especially when alumina is present as impurity, may not occur unless the glass is held at the proper temperature for a long time and when it starts it increases with time so that successive viscosity measurements are not the same.

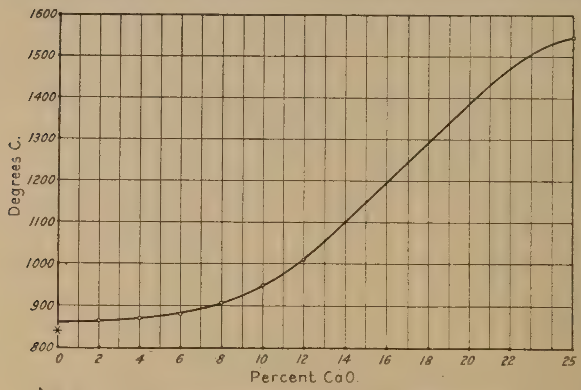

FIG. 8.—Aggregation temperature as a function of CaO.

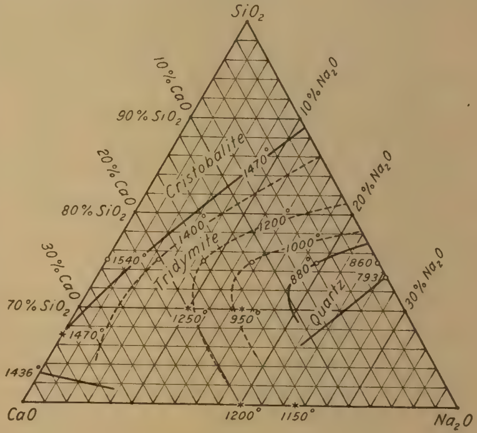

FIG. 9.—Equilibrium triangle for system $CaO–Na_2O–SiO_2$.

Part of the equilibrium triangle for the system Na_2O–CaO–SiO_2 is given in Fig. 9. The limits of the cristobalite and tridymite regions have been determined for calcium silicates and for sodium silicates but nothing is known about the interior of the triangle. Assuming that the aggregation temperatures given by the viscosity curves are the same as the devitrification temperatures, we have now for 75% SiO_2 points on the isothermal curves for 880° (boundary between quartz and tridymite), 1000° and 1200°. Also the points for 1400° and 1470° (boundary between tridymite and cristobalite) may be taken from Fig. 8. This allows us to sketch in roughly the isotherms as shown in Fig. 9.[1] Two points for 70% SiO_2 obtained from the curves of Washburn *et al.* (see Fig. 11 below) are also used in drawing these curves. The two points for 60% SiO_2, also obtained from Washburn *et al.*, probably lie outside the tridymite regions. This figure shows how viscosity and similar measurements may help in the determination of the isothermals of such systems.

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[1] G. A. Rankine, *Amer. Jour. Sci.*, **39**, 5 (1915).

Washburn *et al.* also determined the viscosity curves of a number of soda-lime silicates. Their results for the change of $\log_{10} \eta$ due to substitution of 10% and 20% CaO for Na_2O in glasses with 60, 65, 70 and 75% SiO_2, are shown in Fig. 10. The dashed curves are for actual glasses, the full line curves are from the smoothed isotherm plots. It should be noted that since the change of $\log_{10} \eta$ is obtained by subtracting the value of $\log_{10} \eta$ for the sodium-silicate glass from that for the soda-lime-silica glass, this change is independent of the absolute values and is the same whether we subtract 0.60 from all the W values or not.

In Fig. 10A the curve obtained by English for 10% CaO and 75% SiO_2 is given for comparison. The corresponding W curve is evidently quite different, showing a maximum where the E curve has a minimum. Each of the W curves for 10% CaO except that for 70% SiO_2 shows no indication of a bend upward but rather a tendency to decrease with decreasing temperature below 100°. However in Fig. 10B, the curves for substitution of 20% CaO show bends corresponding to those of the E curves. The corresponding aggregation temperatures are indicated on the equilibrium triangle Fig. 9.

In Fig. 11 are plotted some W values for the change of $\log_{10} \eta$ per per cent CaO, together with the E curve for 10% CaO from Fig. 7. It is remarkable that the left hand straight parts of the curves for 70% SiO_2, 20%

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[1] Note added May 1. Dr. Morey has recently shown me an equilibrium diagram he has prepared on the basis of determinations of the devitrification temperatures of many pure soda-lime silicates. The results will be ready for publication soon. His curve corresponding to Fig. 8 is below mine for less than 10 per cent CaO and above mine for higher percentages. The difference may be due to impurities present in the glasses used for viscosity measurements. Fig. 9 is found to be only a rough approximation, as was to have been expected.

CaO; 60% SiO_2, 20% CaO; 60% SiO_2, 15% CaO and 75% SiO_2, 10% CaO (English) all have about the same slope. The curve for 65% SiO_2, 20% CaO is anomalous. The increase of the change of $\log_{10} \eta$ per degree decrease of temperature seems then not only proportional to the per cent of CaO substituted but independent of the per cent SiO_2.

A striking difference between the E and W results, as shown in Fig. 11, is that above the aggregation temperatures the E curves slope up whereas the W curves slope down, so that at 1400° C the effect per per cent CaO of substituting 10% CaO is .07 according to English (75% SiO_2) and only .004 (70% SiO_2) according to Washburn *et al.* The W results also indicate that the effect at 1400° of substituting lime decreases with decreasing percentage of SiO_2 until for 60% SiO_2 it is practically zero.

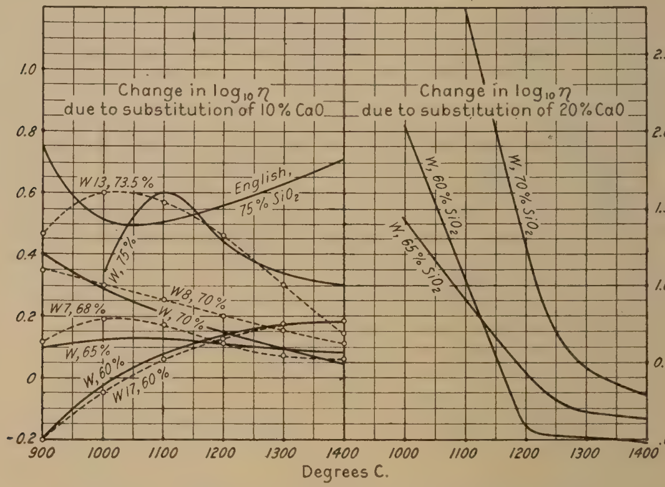

FIG. 10.—Percentage substitution of CaO for Na_2O.

3. Soda-Magnesia-Silica Glasses

English studied four glasses derived from the soda-tri-silicate 1E by molecular substitution of about 0.3, 0.6, 0.9 and 1.1 molecule of MgO for Na_2O. The percentage compositions are given in Table V.

TABLE V

Glass	MgO, per cent	Na_2O, per cent	Equiv. Na_2O, per cent	SiO_2, per cent	Fe_2O_3, Al_2O_3 and CaO, per cent	Total, per cent
1E	0	25.34	25.34	74.05	0.59	99.98
26E	2.49	22.12	25.61	75.00	.26	99.87
329E	5.09	18.26	25.39	76.30	.74	100.39
32E	7.46	14.55	24.98	78.66	.93	99.80
390E	9.30	11.76	24.80	78.28	.91	100.25

Correcting for the slight variation of the values of the equivalent per cent Na_2O (shown in the fourth column) from that for 1E, the *changes of* $\log_{10} \eta$ *due to molecular substitution of MgO and* Na_2O for the various percentages of MgO were determined. These are plotted in Fig. 12A. The full line curves correspond to the curves of Fig. 12B for the change of $\log_{10} \eta$ per per cent MgO. The curves of Fig. 12B show the same type of bend at the aggregation temperature, the same increase of aggregate temperature with per cent substituted and the same constancy of slope below the aggregate temperatures, as the corresponding CaO curves. The experimental results are more irregular, however, and leave us in doubt as to whether the curves for temperatures above the aggregation temperature rise or fall with increasing temperature, and also whether the lines continue straight below 700° or curve down as indicated.

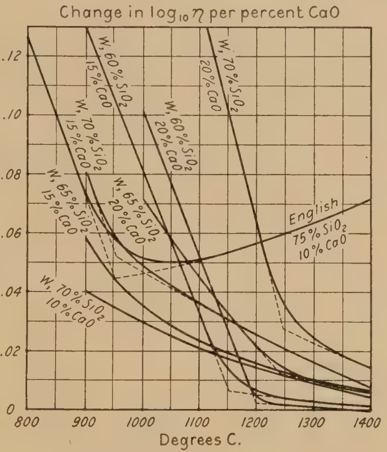

FIG. 11.—Substitution of CaO.

4. Soda-Alumina-Silica Glasses

The two glasses investigated by English had the compositions given in Table VI, being approximately produced by the substitution of .34 and .63 molecule of Al_2O_3 for Na_2O in glass 1E.

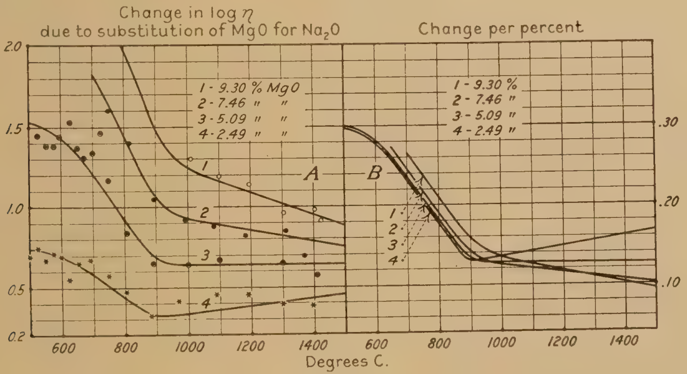

FIG. 12.—Molecular substitution of MgO for Na_2O.

TABLE VI

Glass	Al_2O_3, per cent	Na_2O, per cent	Equiv. Na_2O, per cent	SiO_2, per cent	CaO and Fe_2O_3, per cent	Total, per cent
1E	0.24	25.34	25.48	74.05	0.35	99.98
443E	6.85	20.62	25.52	72.05	.20	99.72
446E	12.69	15.28	24.39	71.56	.31	99.84

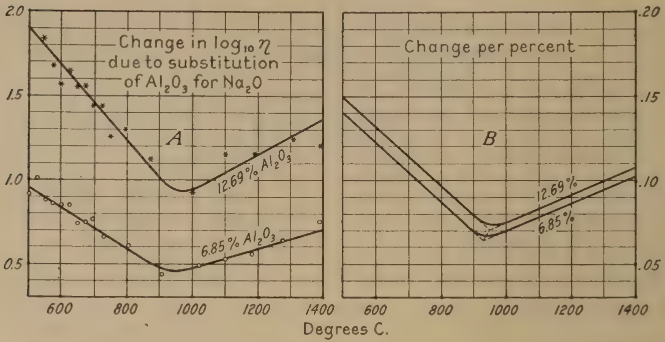

FIG. 13.—Molecular substitution of Al_2O_3.

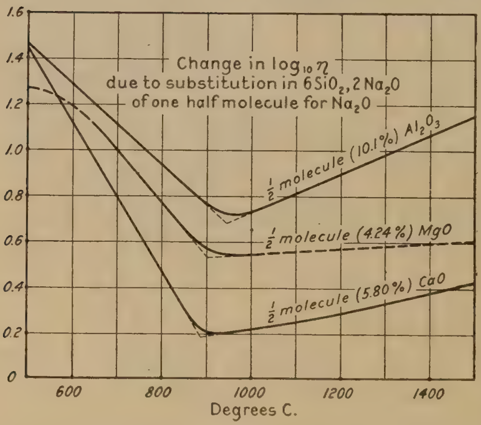

FIG. 14.—Molecular substitution of $^1/_2$ molecule.

The observed changes of $\log_{10} \eta$ due to molecular substitution of Al_2O_3 for Na_2O, corrected for the variation of equivalent Na_2O, are plotted in Fig. 13A. The full line curves correspond to the curves of Fig. 13B for the change of $\log_{10} \eta$ per per cent Al_2O_3. These curves of 13B are evidently similar to the corresponding curves for CaO and MgO. The straightness of the curves of Fig. 13A below 900° and the equality of slope of the curves of Fig. 13B below 900° are as striking as for CaO.

The relative effects of the substitution for Na_2O in ($6SiO_2$, $2Na_2O$) of $^1/_2$ molecule of CaO, MgO and Al_2O_3 are shown in Fig. 14. The three curves are strikingly similar. The Al_2O_3 produces the greatest change of $\log_{10} \eta$ at all temperatures, the CaO produces the greatest increase in rate of set-

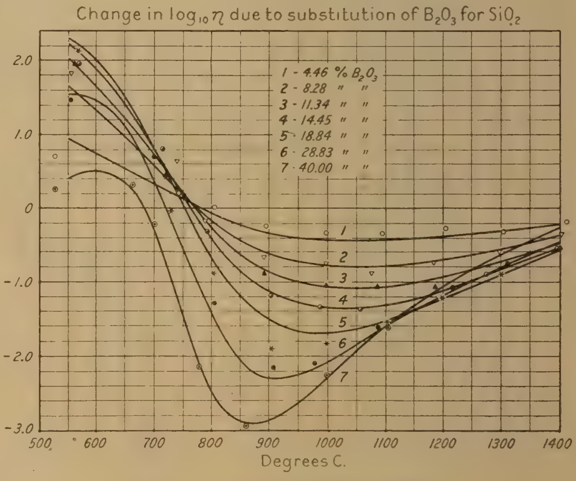

FIG. 15.—Substitution of B_2O_3.

ting at low temperatures, while the effect of MgO is intermediate in both respects. The slopes below 850° are 0.325 (CaO), 0.235 (MgO) and 0.178 (Al_2O_3) per 100°.

5. Soda-Boric Oxide-Silica Glasses

The seven glasses investigated by English were derived from the soda-silicate 600E ($4SiO_2$, $2Na_2O$) by the percentage substitution of boric oxide for silica—not for soda as in previous series—since boric oxide is acidic in character. The compositions are given in Table VII.

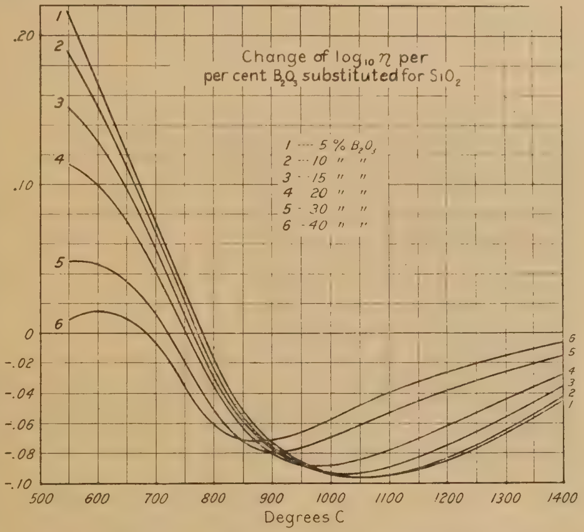

FIG. 16.—Change per per cent due to substitution of B_2O_3.

The change of $\log_{10} \eta$ due to substitution of B_2O_3 for SiO_2 is plotted in Fig. 15 for the seven glasses. The curves are quite different from those for substitution for Na_2O. Above 800° the change is a decrease. Figure 16 gives the change of $\log_{10} \eta$ per per cent B_2O_3 for 5, 10, 15, 20, 30 and 40% B_2O_3. These all show bends at 800° to 1000°, but these are not as sharp as in the case of substitution of Na_2O. The curves below 800° for 5 and 10% B_2O_3 are straight and parallel, but the curve for the higher percentage is on the low temperature side. Perhaps if molecular substitution had been adopted instead of percentage, the curves might have been more similar to each other and to those for molecular substitution of Na_2O.

TABLE VII

Glass	B_2O_3, per cent	SiO_2, per cent	(B_2O_3 + SiO_2), per cent	Na_2O, per cent	Minor per cent	Total per cent
600E	0	79.84	79.84	19.46	0.92	100.22
601E	4.46	74.22	78.68	19.78	1.21	99.67
602E	8.28	71.56	79.84	18.76	1.18	99.78
603E	11.34	68.39	79.73	18.92	1.22	99.87
604E	14.45	64.72	79.17	19.95	0.92	100.04
605E	18.84	61.28	80.12	18.93	0.93	99.98
606E	28.83	50.04	78.87	20.36	0.91	100.14
607E	39.99	35.22	75.21	23.71	1.07	99.99

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OBSERVATIONS ON "HAIRLINES" IN SHEET IRON ENAMELS[1]

By J. E. Hansen and Gordon S. Lindsey[2]

ABSTRACT

Hairlines in sheet iron enamels may be caused either by under-firing of the ground coat enamel, or by "cold spots" on the ware when the cover enamel is fired. The defect may be prevented by properly firing the ground coat enamel, and by proper arrangement of the ware on the firing supports in the furnace.

By "hairlines" in sheet iron enamels, the authors refer to that defect which appears in sheet iron enamels applied by the wet process, and which is characterized by very fine black lines in the cover coat enamel, where the dark under-coat, either ground coat or dark colored edging enamel, shows through the cover enamel in a "hairline" formation. These hairlines usually appear in a more or less parallel conformation, but may spread out radially into a fan-shaped figure. This defect is sometimes called crazing, but wrongly so.

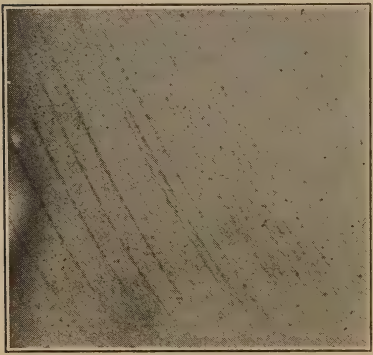

Fig. 1.—Typical example of hairlines.

Crazing is characterized by fine *cracks* in the enamel, which appear while the enamel is cooling, or some time after it is cool. "Hairlines," however, are simply *lines* in the enamel, not cracks, and appear during the firing or fusing of the enamel.

A typical example of hairlining such as appears on stove parts is shown in Fig. 1. This piece of ware has a ground coat, a black edging enamel, and two coats of white enamel. The hairlines on this piece appeared during the firing of the second coat white enamel, but they sometimes appear

Fig. 2.—Cross-section of enamel ware, showing hairlines as raised ridges in undercoat of enamel.

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, February, 1925. (Enamel Division.)

[2] Industrial Fellows of the Mellon Institute of Industrial Research of the University of Pittsburgh, Pittsburgh, Pa.

in the first white coat, and in a few instances have been visible in the black edging enamel.

A cross-section of a piece of enamelware showing these hairlines is given in Fig. 2. This shows the dark undercoats of enamel raised up in a ridge into the white enamel, coming so near the surface that the black ridge shows through as a dark hairline.

Hairlines are known to have appeared on almost all classes of sheet iron enamelware, including hollow ware, signs, table tops, stove parts, and other products.

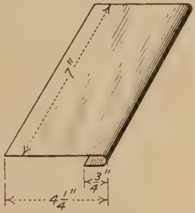

FIG. 3.—Type of test piece used.

Observations

Various conditions under which hairlining has appeared have been observed by the authors, and in trying to arrive at an idea of the cause of such defects, and a possible remedy, certain trials were made to purposely cause hairlines in the enamel.

Standard test pieces of 22 gage Armco iron, 5 x 7 inches, were cut and one edge bent over as shown in Fig. 3 to roughly approximate a gas stove shelf with a rolled edge. Thirty of these pieces were properly cleaned and pickled, and ground coat enamel was applied. Fifteen pieces were fired at 1600°F for four minutes, while fifteen were fired for three minutes at the same temperature. All the trials fired for four minutes were fully matured, as judged by the color of the ground coat, while those fired for three minutes were slightly underfired, but would have passed the usual factory inspection as properly fired.

FIG. 4.—Showing hairlines in underfired enamel over the rolled edge of the sample.

When cool, these pieces were sprayed with a thin coat of "black edge enamel," which was then fired at 1600°F for one and one-half minutes, at the end of which time the enamel had a good gloss.

Two coats of white enamel were applied, edges being brushed back on each coat, leaving a $^{1}/_{4}$-inch black edge. Both coats of white were fired for two minutes at 1500°F. No hairlining was visible to the naked eye in any of the trials after the first coat of white was fired.

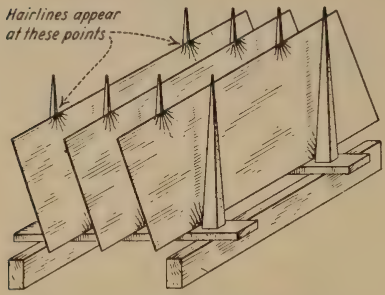

Fig. 5.—Showing hairlines of the type caused by cold firing supports.

After firing the second coat of white enamel, the trials were again examined. In the lot of fifteen pieces which had been fired for four minutes in ground coat, there was only one piece showing hairlining. In the lot of fifteen pieces fired for only three minutes in ground coat, nine pieces showed quite a few hairlines, while two others showed traces of hairlines. The hairlines were for the greater part immediately over the "rolled-over edge" of the trial piece, where the double thickness of metal which had to be heated in the furnace had contributed even more to the underfired condition of the enamel on that portion of the piece. Fig. 4 shows a portion of one of these pieces showing hairlines.

This portion of the experimental work checks closely the results obtained in a plant making enameled signs, where hairlining was encountered on a circular sign of a diameter of about three feet. It had been the plant practice to fire these signs three on a load in all firings, and about one-third of the signs showed hairlining in the cover enamel. On a few trial runs, careful record was kept of the position of each sign in the enameling furnace, and it was observed that it was the sign which had been fired in the cooler end (the door end) of the furnace which showed the hairlines. On the assumption that it was the less fired ground coat from the cool end of the furnace which later caused this trouble, the plant practice was changed so that two signs were fired on a load in ground coat enamel, and three signs as usual in all following

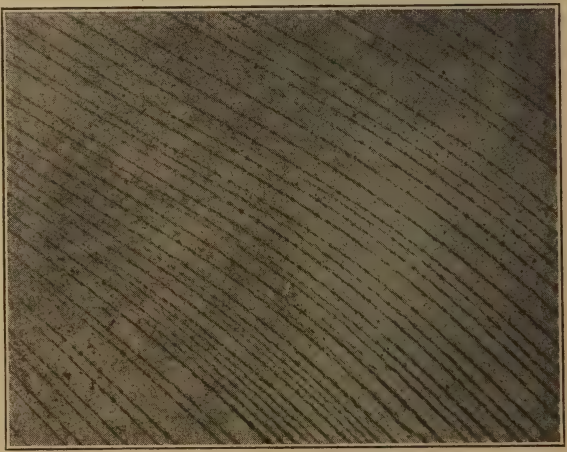

Fig. 6.—Hairlines caused by placing cold block of iron under the sample when cover enamel was fired.

coats. With this change in firing practice, almost all the hairlining disappeared.

Hairlining sometimes also appears in the corners of broiler pans in stove work, where the ground coat enamel has not properly drained away. This heavy deposit of ground coat is then usually not fired down properly, and hairlines show up in that region in the later coats of enamel.

Hairlines have also been encountered in several enameling plants on "double faced" flatware, which, because of the necessity of avoiding firing-pin marks, had to be fired on racks against which the ware was leaned, as shown in Fig. 5. These racks are of rather rugged construction, and although preheated in the furnace, they lose considerable heat before they can be loaded with ware and put back into the furnace. Consequently the supports against which the ware leans are somewhat cold, and heat up more slowly than the ware itself. Hairlines often show up in the enamel, at the point indicated in Fig. 5.

In the discussion on hairlining at the 1924 meeting of the Enamel Division of this SOCIETY at Atlantic City, it was brought out that one hollow-ware enameling plant had experienced hairlining on that portion of the body of a coffee pot which was in close proximity to the handle of an adjacent coffee pot, as the ware was placed on the firing points. A different arrangement of the ware in the furnace, affording a wider spacing between each pot and the handle of the adjacent pot, eliminated the hairlines.

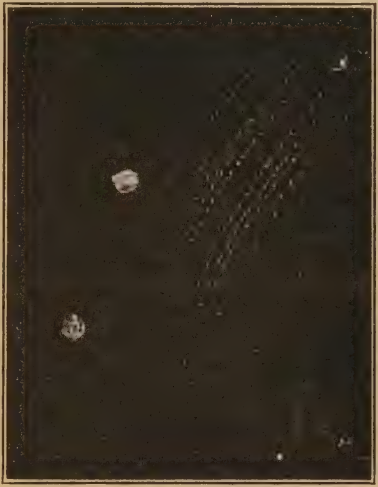

FIG. 7.—Hairlines in ground coat caused by placing cold block of iron under ware when cover enamel was fired.

The authors duplicated this type of hairlining in an experimental way by placing a cold block of wrought iron between the firing points, directly underneath and close to the enameled pieces being fired, leaving about $^1/_4$ inch clearance. When firing ground coat with this chunk of cold iron underneath the ware, the enamel was slightly underfired at that spot, but not enough so to cause hairlining in the cover coat enamel, if the latter was fired in the usual manner.

However, if the cold piece of iron was placed beneath the ware when the cover enamel was fired, the latter was found to be badly hairlined. These hairlines are shown in Fig. 6.

Several pieces which were made to hairline by placing the cold iron near the ware, also showed hairlines on the back side, that is, in the ground coat itself. Such a case is shown in Fig. 7. The peculiar part of this feature is that the hairlines on the reverse side of the piece run at right angles to the hairlines on the other side of the piece. No explanation is offered for this behavior.

Summary

These trials show that there are at least two conditions under which hairlines will appear in enamels, namely, from an underfired ground coat enamel, and from "cold spots" caused by contact with, or close proximity of the enameled ware to cold objects as it is fired in the furnace.

The underfired ground coat may be the result of too short a firing time, too low a firing temperature, or of too thick enamel, in which case the problem resolves itself into properly setting up the enamel before dipping and firing.

The remedies to be suggested are quite obvious.

Proper firing of the ground coat will eliminate much of the hairlining from the underfiring factor. This may entail firing smaller loads of ware, to insure that it is all properly fired. In the case of ware having rolled edges, or double thicknesses of metal which absorb heat more slowly than other sections, it might be advisable to remove the ware from the furnace for a few seconds after it has reached red heat and allow the thin sections to cool, and then run it back into the furnace until the ground coat is fully matured. Likewise, firing the ground coat at a slightly lower temperature than usual for a somewhat longer time would allow the heavier parts of the ware to become properly fired without danger of badly overfiring the balance of the ware.

The elimination of cold firing supports, or placing the ware in a different manner in the enameling furnace, should eliminate hairlining due to unequal heating in the finish coats of enamel.

A STUDY OF THE FACTORS INVOLVED IN THE SPALLING OF FIRE CLAY REFRACTORIES WITH SOME NOTES ON THE LOAD AND REHEATING TESTS AND THE EFFECT OF GRIND ON SHRINKAGE[1]

By M. C. Booze and S. M. Phelps[2]

ABSTRACT

Of the three factors, elasticity, coefficient of expansion and rate of temperature change, which affect spalling, the former is by far the most important. Only small differences are found between fire clay mixtures of widely varying structure and composition in the rate at which they change in temperature under like conditions of heating. The coefficient of expansion varies directly with the silica content and differences in this respect of large order were found. However, the spalling on the particular mixtures tested varied almost inversely as the coefficient of expansion. This apparent discrepancy is explained on the basis of greater elastic properties of the brick which had high expansions. The elasticity may be varied between wide limits and is sufficiently important as to overbalance the effect of greater expansion. This property is accordingly the one upon which efforts directed toward the development of non-spalling brick should be centered. It was discovered that a plastic deformation could be obtained at as low a temperature as 635°C. This gives the effect of elasticity and undoubtedly has considerable influence on spalling at the higher temperature ranges.

Results are given for a number of load tests which show clearly the importance of hard firing. The secondary expansion of brick made from Pennsylvania flint clay is shown to be influenced by the temperature of reheating, as well as its rate.

Detailed results showing the effect of grind and firing on the finished size of the brick included in the investigation are also given.

This study suggested itself through a consideration of the relation of spalling to the physical properties of fire clay refractories. It was known that such factors as hard and soft firing, coarse and fine grinding, introduction of grog or calcine, replacement of plastic clay by flint clay, open and dense firing clays, and to some extent the chemical composition were of considerable importance in accelerating or retarding spalling. It was not known, however, how variations in these factors affected individual properties of the refractories, nor the relative importance of those physical properties which govern spalling.

The stresses in a brick obviously arise from unequal expansion, which is in turn due to temperature differences of adjoining parts. If the brick is sufficiently elastic, the stresses due to differential expansion will merely produce a readjustment of the individual particles without causing fracture. Should the amount of expansion be enough, however, to cause the elastic limit and ultimate strength to be exceeded, breakage will take place.

It is evident that resistance to spalling can be increased by decreasing the coefficient of expansion, and by increasing the elasticity, strength and heat conductivity. A spalling formula based on these factors is possible of development, but its value and accuracy would be most questionable. This investigation will have served its purpose if it indicates the relative amount of variation of the different factors which may be produced in practical ways and the corresponding effect upon the finished product.

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, February, 1925.

[2] Industrial Fellows, Multiple Industrial Fellowship of the Refractories Manufacturers Association, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

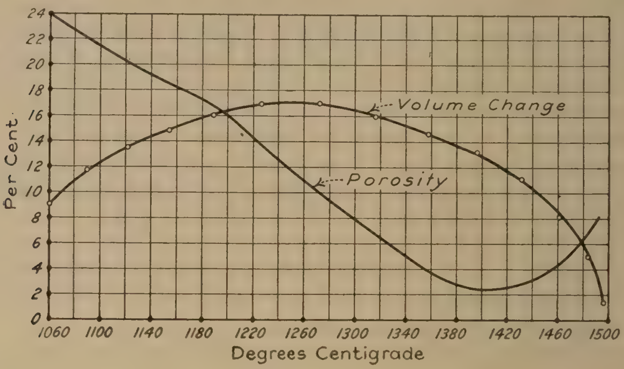

FIG. 1.—"K" plastic clay.

Such information is necessary in order that investigations on the production of a non-spalling brick may be conducted in an efficient manner.

In the past it has been exceedingly difficult to obtain accurate information on the behavior of various classes of fire clay refractories in industrial furnaces. Because of inconsistencies and discrepancies in reports made by various observers, it has not been possible to reach intelligent conclusions from service data. In addition to spalling, breakage may occur from the fact that the brick are improperly laid and subjected to bending stresses or from pinching off of the inner ends when the face of the lining expands. In some cases the brick or refractory shapes have been laid up dry or only loosely bonded and broken pieces fall out more readily than would be the case with better construction. In one instance hand made and relatively uneven shapes were laid dry in an arch with large, open joints and spalled badly because of the exposure of several faces to the heat.

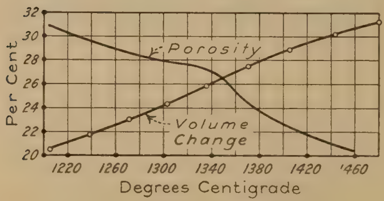

FIG. 2.—"W" plastic clay.

In some oil-fired furnaces a rapid disintegration of the refractories takes place. It is not known whether this is due to spalling or to some peculiar effect of the oil. The bungs of malleable iron furnaces are supposed to furnish a typical example of spalling conditions and yet service reports are most conflicting. Tests have shown that the bung brick are often subjected to an enormous initial stress from the set screws used to hold them in the frame and it is reasonable to suppose that this stress may be increased to the crushing point by the normal thermal expansion. Under conditions such as have been described, it is difficult to study this cause for failure and accordingly laboratory tests must be largely relied upon in the development of brick with true low spalling tendencies.

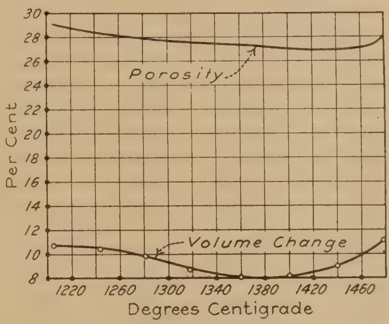

FIG. 3.—"M" flint clay.

Preparation of Test Pieces

As it was highly desirable to keep the investigation within the bounds of practical limits, the aid of a fire brick company was obtained in preparing the samples. The Kier Fire Brick Company, through its president, S. M. Kier, gave the fullest coöperation in this respect and aside from having the pieces manufactured for this investigation, gave other advice and assistance which has been most valuable.

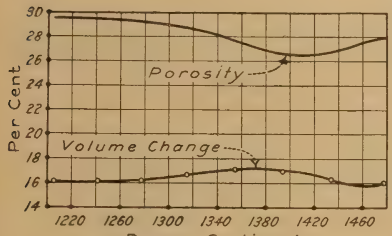

FIG. 4.—"S" flint clay.

Table I identifies the various samples as to grind, firing, composition and method of manufacture. Screen analyses of the green mixtures are given in Table II, chemical composition of the clays used in Table III, and the results of firing tests in Table IV. These firing properties are also shown graphically in Figs. 1, 2, 3, 4 and 5.

The mixtures from 1 to 9 inclusive were prepared by grinding the various batches in a wet pan, sufficient mud from each batch for the specimens of coarse grind being taken out at the proper time and the balance in the pan then further ground for the samples of fine grind. In this way, the composition was kept the same for all samples in one lot. The mud was molded into 9-inch brick and cylindrical rods approximately 10 inches long by $1^1/_{16}$ inches in diameter, the latter being for coefficient

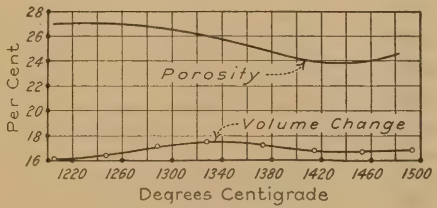

FIG. 5.—"D" flint clay.

of expansion measurements. The brick were not repressed after molding in order that their density and structure would be like that of the rods.

TABLE I

IDENTIFICATION OF MIXTURES TESTED

Mark	Grind	Firing	Method of manufacture		Composition
1FS	Fine	Soft	Cone 3	Soft mud	100% "K" clay
1FH	Fine	Hard	Cone 12		
1CS	Coarse	Soft	Cone 3		
1CH	Coarse	Hard	Cone 12		
2FS	Fine	Soft	Cone 3	Soft mud	80% "S" flint; 20% "K" plastic
2FH	Fine	Hard	Cone 12		
2CS	Coarse	Soft	Cone 3		
2CH	Coarse	Hard	Cone 12		
3FS	Fine	Soft	Cone 3	Soft mud	80% "S" flint; 20% "W" plastic
3FH	Fine	Hard	Cone 12		
3CS	Coarse	Soft	Cone 3		
3CH	Coarse	Hard	Cone 12		
4FS	Fine	Soft	Cone 3	Soft mud	80% "D" flint; 20% "K" plastic
4FH	Fine	Hard	Cone 12		
4CS	Coarse	Soft	Cone 3		
4CH	Coarse	Hard	Cone 12		
5FS	Fine	Soft	Cone 3	Soft mud	80% "D" flint; 20% "W" plastic
5FH	Fine	Hard	Cone 12		
5FS	Coarse	Soft	Cone 3		
5FH	Coarse	Hard	Cone 12		
6FS	Fine	Soft	Cone 3	Soft mud	80% "M" flint; 20% "K" plastic
6FH	Fine	Hard	Cone 12		
6CS	Coarse	Soft	Cone 3		
6CH	Coarse	Hard	Cone 12		
7FS	Fine	Soft	Cone 3	Soft mud	80% "M" flint; 20% "W" plastic
7FH	Fine	Hard	Cone 12		
7CS	Coarse	Soft	Cone 3		
7CH	Coarse	Hard	Cone 12		
8FS	Fine	Soft	Cone 3	Soft mud	80% calcined "S" flint; 20% "K" plastic
8FH	Fine	Hard	Cone 12		
8CS	Coarse	Soft	Cone 3		
8CH	Coarse	Hard	Cone 12		
9FS	Fine	Soft	Cone 3	Soft mud	70% "M" flint calcined; 10% "K" plastic calcined; 20% "K" plastic raw
9FH	Fine	Hard	Cone 12		
9CS	Coarse	Soft	Cone 3		
9CH	Coarse	Hard	Cone 12		
10H	Medium	Hard	Cone 12	Auger machine repressed	71% "M" flint; 29% "K" plastic
10S	Medium	Soft	Cone 3		
11H	Medium	Hard	Cone 12	Hand made	70% "M" flint raw; 4% "M" flint calcined; 26% "K" plastic raw
11S	Medium	Soft	Cone 3		

TABLE II

SCREEN ANALYSES OF GREEN MIXTURES MADE WET ON STANDARD SIEVES

Mixt.	On 4-mesh screen	Through 4 on 10	Through 10 on 20	Through 20 on 40	Through 40 on 60	Through 60 on 80	Through 80 on 100	Through 100-mesh screen
2F	0 %	5.7%	17.7%	15.0%	6.4%	3.7%	1.5%	49.0%
2C	28.5	24.7	10.4	7.7	3.4	1.9	0.9	22.4
3F	0	5.5	14.9	30.2	7.7	4.5	2.1	35.0
3C	20.5	26.6	10.8	8.0	4.0	2.4	1.2	26.4
4F	0	8.7	21.7	14.4	4.9	2.9	1.4	45.8
4C	30.5	20.6	7.9	6.2	2.6	1.7	0.9	29.5
5F	0	9.5	22.2	15.5	5.8	3.9	2.3	40.8
5C	38.9	17.6	7.6	4.7	2.8	1.8	1.1	25.4
6F	0	8.0	20.0	11.4	6.3	3.9	2.1	48.0
6C	19.3	20.4	9.6	7.9	4.0	2.5	1.5	34.7
7F	0	6.2	16.9	14.3	6.7	3.7	2.4	53.9
7C	14.3	24.6	11.4	8.5	4.6	3.2	1.8	41.5
8F	0	2.18	14.3	23.5	10.2	4.6	2.8	42.3
8C	21.9	19.7	12.6	15.1	4.6	2.2	1.0	22.9
9F	0	4.9	18.8	17.2	8.2	4.0	2.2	44.6
9C	7.7	22.5	17.8	13.4	5.5	3.0	1.5	28.4
10	0	17.5	17.5	12.0	4.8	2.6	1.2	44.2
11	2.0	23.7	13.3	9.9	4.4	2.3	1.1	32.2

TABLE III

CHEMICAL ANALYSES AND FUSION POINTS OF CLAYS INCORPORATED IN SPECIMENS TESTED

	"D" Flint clay	"S" Flint clay	"M" Flint clay	"K" Plastic clay	"W" Plastic clay
SiO_2	50.61	53.64	45.69	56.65	65.25
Al_2O_3	45.33	42.35	46.34	36.33	29.46
TiO_2	2.44	2.09	3.34	2.95	2.30
Fe_2O_3	0.77	1.12	2.73	1.79	2.07
CaO	0.26	0.35	0.29	0.35	0.28
MgO	0.10	0.19	0.21	0.66	0.28
Alkalis	0.24	0.17	1.12	1.23	0.29
Fusion point, cone	33–34	33–34	33	30–31	32

TABLE IV

FIRING PROPERTIES OF CLAYS

Clay	"W" Plastic clay	"K" Plastic clay	"S" Flint clay	"M" Flint clay	"D" Flint clay
Drying shrinkage		19.5%	8.8%	8.9%	9.1%
Water of plasticity		19.4	17.4	16.4	17.4
Fired porosity:					
Cone 6 1205°C	31.0%	See	29.5	29.1	27.0
8 1275	28.6	figures	29.2	28.4	26.9
10 1325	27.5	below	28.5	27.7	25.9
12 1370	24.5		27.2	27.4	25.2
16 1460	20.5		27.6	27.1	23.9
18 1480	19.3		27.8	28.0	24.6

TABLE IV (*Continued*)

Clay	"W" Plastic clay	"K" Plastic clay	"S" Flint clay	"M" Flint clay	"D" Flint clay
Volume shrinkage:					
Cone 6	20.5		16.1	10.7	16.1
8	23.1		16.1	10.3	16.6
10	24.9		16.9	8.5	17.5
12	27.7		17.2	8.1	17.3
16	30.2		16.0	9.8	16.8
18	31.3		16.2	11.0	16.8

"K" PLASTIC CLAY

Cone	Temperature	Volume change	Porosity
.	1060°C	9.1%	24.0%
.	1100	12.4	21.6
1	1160	14.9	18.2
3	1205	16.0	17.6
5	1250	18.4	10.5
9	1312	15.9	4.8
13	1357	14.6	4.0
15	1415	12.4	2.3
17	1455	4.6	4.5
.	1495	1.6	8.3

Firing was accomplished in a periodic kiln according to the usual plant practice. The soft and hard firings were obtained by placing in different positions in the kiln.

Laboratory Tests

Coefficient of Expansion

For these determinations, a furnace was designed and built by the junior author. A detailed drawing of this is given in Figs. 6 and 7. It was originally intended to make the determinations at temperatures as high as 1350°C and it was for that reason that a gas fired furnace was used. It was found, however, that the fused silica rods which connected the test specimen with that part of the apparatus which was used for indicating expansion, softened so badly above 1125°C that the test could not be conducted at higher temperatures. This condition was also noted by Mer-

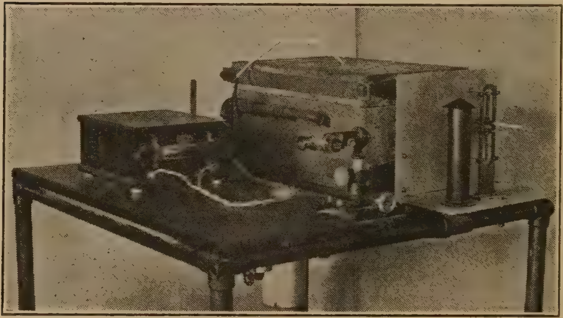

FIG. 6.

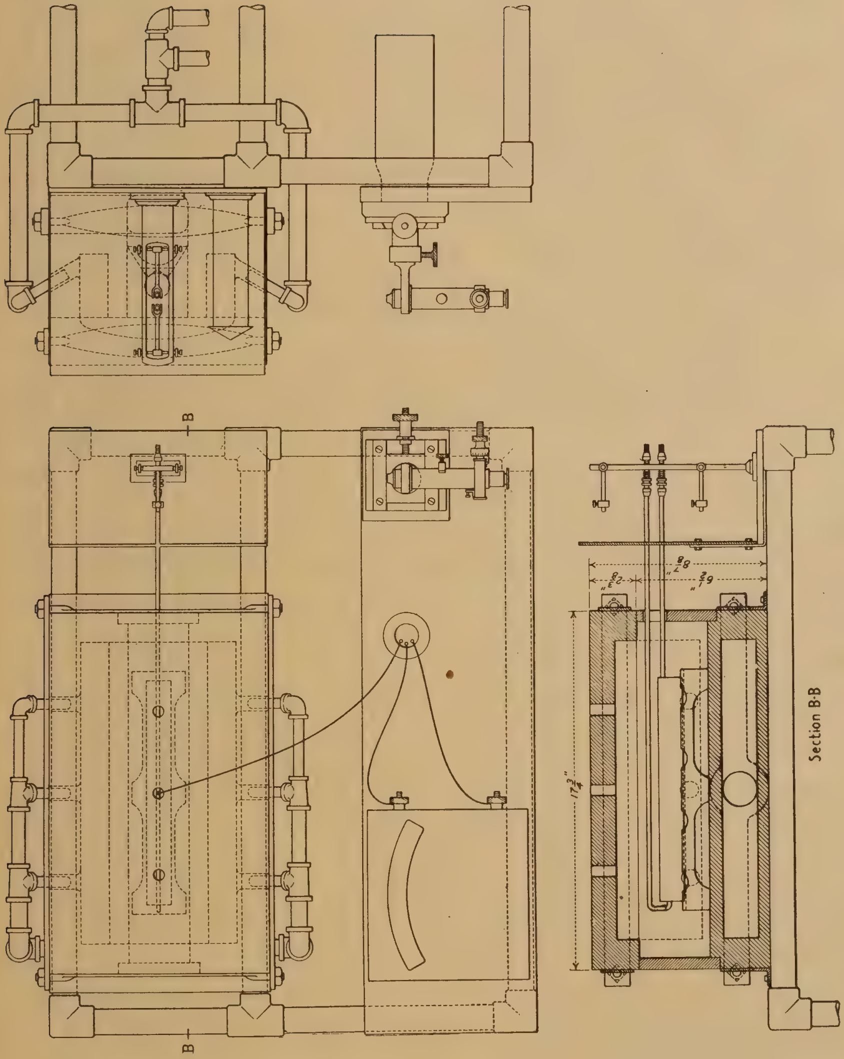

FIG. 7.

ritt[1] and reported at about the same time these tests were being conducted. A partial analysis made on one of the rods which deformed badly showed a silica content of only 96.3%, which may explain the premature softening.

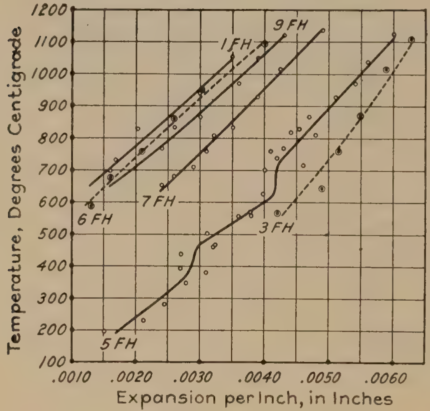

Fig. 8.—Reversible expansion of various clay mixtures.

On account of this softening, the expansion was not determined during the heating-up period, except over low temperature ranges. At the highest temperatures the thermal contraction was obtained by taking an initial reading and allowing the temperature to fall rather rapidly to a point where the silica glass would be rigid. The cooling schedule between 1000°C and 500° required approximately five hours, the furnace then being allowed to cool down over night before a final reading was taken. By using high bag walls and down-draft in the furnace, with the flame playing on a bed of granular material, good combustion and a uniform temperature distribution were obtained. While the temperature range for the test was limited by softening of the quartz rods, errors from this cause were minimized by taking readings only during the cooling period. The expansions were read to $^1/_{1000}$ inch by means of a Filar micrometer eyepiece in the microscope, and, as the maximum expansion varied from .040 to .075 inch, the error from lack of sensitiveness was not extreme.

The expansions of the various mixtures tested with corrections made for the normal expansion of the silica rods are given in Figs. 8, 9, 10 and 11. The results for the temperature ranges from 0 to 800°C, 800 to 1100°C and 0 to 1100°C are also given in Table V.

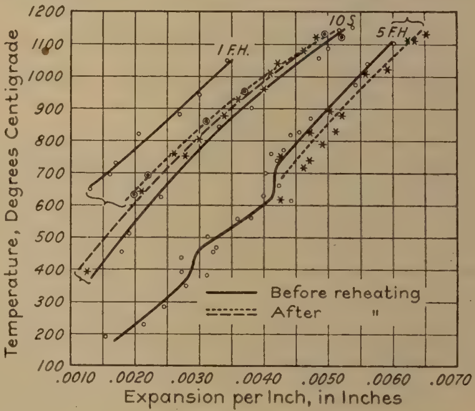

Fig. 9.—Effect of reheating on the reversible expansion of clay mixture.

The various mixtures differed to a greater extent in this property than was expected and also showed lower average coefficients than previously

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[1] "Thermal Expansion of Fused Quartz," *Jour. Amer. Ceram. Soc.*, 7 [11], 803 (1924).

TABLE V

AVERAGE COEFFICIENTS OF EXPANSION[1]

Mixt.	0 to 1100°C	800°C to 1100°C	0 to 800°C
1FH	2.6	3.0	2.2
1FH reheated	3.9	4.1	3.1
7CH	4.0	4.2	3.7
7FH	4.1	4.2	3.3
7FH reheated	5.7	5.6	6.1
5FH	5.7	5.4	5.9
5FH	5.8	5.4	6.1
5FH reheated	5.7	5.6	6.1
5FH reheated	5.9	5.7	6.3
3FH	6.4	5.8	7.3
6FH	3.1	3.37	2.4
10S reheated	4.0	4.0	3.7
10S reheated	4.5	5.0	3.3
10S	4.2	4.2	4.1
10H	4.1	4.2	3.4
9FH	3.5	3.6	2.8

published results have indicated. The amount of expansion between 0° and 650°C bears a relation to the silica content and is also governed to a small degree by the temperature of firing. The effect of silica on the expansion is shown in Fig. 11. The only result not falling on this curve was obtained on 1FH which was made entirely from plastic clay and which probably contained a much larger proportion of glass than the other samples. The effect of firing temperature is shown in Fig. 9, in two cases the expansion being increased by harder firing and decreased in a third. The effect of successively higher firing temperatures has been shown by Houldsworth and Cobb,[2] who obtained values both lower and higher than that of the original sample. The lowest value of all was obtained when the test piece was fired at an extremely high temperature and which in all probability produced a large amount of glass.

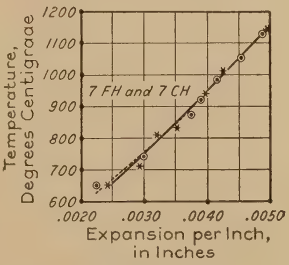

FIG. 10.—Effect of grind on the reversible expansion.

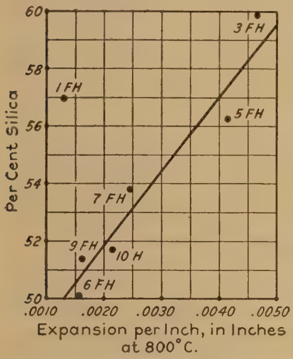

FIG. 11.—Effect of silica on the reversible expansion.

From the results shown graphically in Fig. 10 it is apparent that the grind has no effect on the thermal expansion.

Instead of the value 0.0000075 which has ordinarily been used in computing the expansion for furnace design, values from 0.000004 to 0.000006 should be used for brick with silica contents varying from 50 to 60%, the low value being used for the low silica content.

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[1] To get correct values, multiply figure given by 10^{-6}.

[2] "The Reversible Expansion of Refractory Materials," *Jour. Amer. Ceram. Soc.*, **6**, 645–662 (1923).

Diffusivity or Rate of Temperature Change

While the heat conductivity is of importance in determining the temperature gradient within a body, the property which is desired here involves the specific heat and density as well. During the heating or cooling the maximum temperature gradient will be greater than when equilibrium is reached, due to the heat capacity of the body. Since it is the temperature difference which determines the amount of stress with a given coefficient of expansion, it is obvious that the factor which should be determined in this investigation is one of temperature difference with the body in an unsaturated condition.

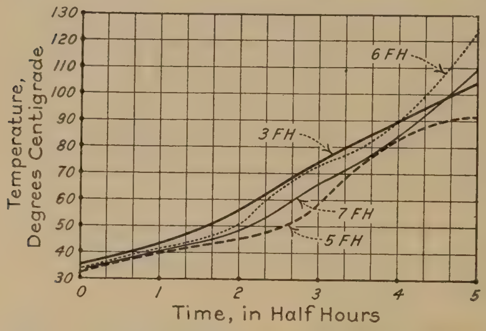

FIG. 12.—Rate of temperature increase as result of heat transmissions through 8 inches of brick, with hot end at 1050°C.

In making this determination several 9 x $4^1/_2$ x $2^1/_2$-inch brick were built into a panel, each brick being separated from the adjoining one by a $1^1/_4$-inch layer of Sil-O-Cel brick and all joints made tight with a plastic insulating cement. In this panel the $2^1/_2$ x $4^1/_2$-inch faces of the test brick were exposed, holes being drilled in the opposite ends to a depth of one inch and these filled with mercury. An open top, gas-fired furnace, whose horizontal cross-section was somewhat larger than the panel of test brick was partially filled with granular refractory material and this heated to a uniform surface temperature of 1000°C by the "surface combustion" principle. The test panel was then placed over the furnace and temperatures taken at intervals on the cold ends of the brick by means of thermometers placed in the mercury wells. These temperatures are given in Table VI and are shown graphically in Figs. 12 and 13.

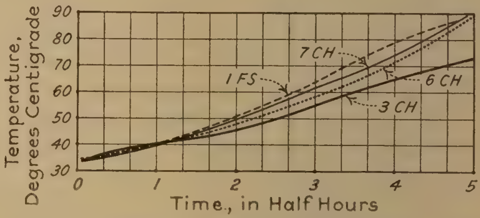

Fig. 13.—Rate of temperature increase as result of heat transmission through 8 inches of brick with hot end at 1050°C.

By reference to these data, it will be seen that the differences between the various mixtures are quite small. The finely ground brick show slightly

TABLE VI

DIFFUSIVITY OR RELATIVE RATE OF TEMPERATURE INCREASE OF FIRE CLAY BRICK

Identification number	Beginning of test	$^1/_2$ hour heating	1 hour heating	$1^1/_2$ hour heating	2 hours heating
3FH	35.5°	43.7°	56°	74.2°	88.7°
7CH	33.5	41.5	49.5	62.2	74.7
6FH	34.2	43	50.7	74.0	92
1FS	33.7	42.7	48.5	63.7	79
5FH	32.7	39.5	45.7	58.5	73
6CH	33.8	42	47.5	58.8	72
3CH	34.3	41.3	46	55.2	64.7
7FH	33.5	40.5	49.5	66.2	84.2
10H	33.5	41.7	48.2	61.0	74
10S	33.2	41.2	48.2	55	74

higher temperatures at the cooler ends than do those of coarse grind. No comparison was made between hard and soft fired samples, those included here being the ones upon which the whole investigation was largely centered.

While it would have been advisable to have made the temperature determinations at various depths in each brick had time permitted, it is not probable that the temperature gradients would have differed materially.

The samples tested represented rather wide extremes in porosity, that marked 1FS having a porosity of 15% and 5FH 26%. The test pieces, accordingly, were of greater variation in structure than would normally be found in commercial products and since the temperature differences were small it does not seem that the structure is of very much importance as far as heat efficiency is concerned in choosing brick to be used for checkers in regenerators.

Elasticity The apparatus used for these determinations is shown in Fig. 14. The test pieces used were 9 x $4^1/_2$ x $2^1/_2$-inch brick, and in each test the specimen was clamped rigidly on one end in the machine and a torque applied at the other by means of weights and a lever. The angle of deflection was read by means of a telescope sighted on mirrors fastened to each end of the brick and which reflected the image of a radial scale fixed at a distance of $28^1/_2$ inches from the center of the brick. By this means it was possible to read the angle of rotation to within 0.0082 of a degree, or a relative motion of the brick of 0.00054 inch at a distance of $2^1/_4$ inches from the center and on points 6 inches apart or the distance between the mirrors. Readings were taken at two temperatures, heating of the specimen being accomplished by nichrome coils and the temperature measured by inserting a thermocouple to a depth of 2 inches in a hole drilled in one end along the center line.

The data obtained in this test are given in Table VII. The results are extremely interesting not only in showing very great differences in elasticity, but also in pointing out the effect of temperature on the elastic properties and in establishing the fact that plastic and permanent deformation takes place at surprisingly low temperatures. This is clearly indicated by the figures in the table and could readily be noted on some of the specimens after they were tested and removed from the apparatus. The stress required to produce this low temperature deformation varied from 75 to 180 pounds per square inch at a temperature of 635°C. This is greater than that which would ordinarily arise in furnaces due to the weight load to which they are subjected. Where the conditions are not such as to bring about an undue amount of settling, the property of having plastic flow at low temperatures may be advantageous. In the case of spalling this softening gives the effect of elasticity and the particles within the refractory body may move under the spalling stresses without cracking taking place and thus the upper limit of the temperature range over which spalling will occur will be determined to a large extent by the softening temperature. Where the brick in a furnace lining or roof are held rigidly in place they are subjected to compressive stresses when heated up due to their thermal expansion and this may cause failure due to pinching or crushing. If, however, they soften sufficiently to flow, the chances for failure are considerably lessened. The early softening which is referred to here and which has been detected in the elasticity test is apparently not one in which all of the clay deforms. It seems rather to be a condition where a small amount of glass which is holding the individual particles together has its viscosity lowered sufficiently that it will give under a stress less than that required to produce rupture. In determining the elasticity as it affects spalling over any temperature range, it is necessary to know the amount that the brick can be strained before rupture takes place. In many of the tests which were conducted here the amount of strain prior to rupture could not be determined due to the softening which took place. With materials of very high viscosity plastic deformation may take place

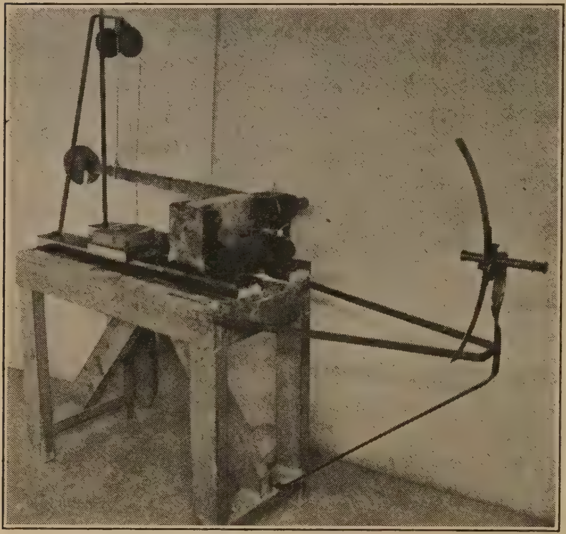

FIG. 14.

Table VII

Elastic and Plastic Deformation of Various Fire Clay Mixtures

Mixt.	Temp.	Weight[1]	Deflection on scale[2]	Elastic deformation	Plastic deformation
3FH	635°C	24 lbs.	$1\frac{1}{2}$	1	$\frac{1}{2}$
3FH	635	30.35	2	1	1
3FH	725	24	$2\frac{1}{4}$	$2\frac{1}{4}$	0
3FH	725	62.15	7	$5\frac{1}{2}$	$1\frac{1}{2}$
3FH	725	68.8	$8\frac{1}{2}$ and broke	. .	. .
3CH	635	5	$1\frac{1}{4}$	$\frac{1}{4}$	1
3CH	635	12.5	8	$4\frac{1}{4}$	$3\frac{3}{4}$
3CH	725	7.5	3	3	0
3CH	725	12.5	10	7	3
3CH	725	18.75	30	$13\frac{1}{2}$	$16\frac{1}{2}$
7FH	635	30.65	$2\frac{1}{4}$	2	$\frac{1}{4}$
7FH	725	30.65	$4\frac{1}{4}$	3	$1\frac{1}{4}$
7CH	635	9	2	2	0
7CH	635	24	$3\frac{1}{4}$	$2\frac{3}{4}$	$\frac{1}{2}$
7CH	635	30.65	$4\frac{1}{2}$	$3\frac{3}{4}$	$\frac{3}{4}$
7CH	725	6.35	$2\frac{1}{4}$	1	$1\frac{1}{4}$
7CH	725	13.0	17	5	12
5FH	800	24	$4\frac{1}{2}$	3	$1\frac{1}{2}$
5FH	800	30	55	$10\frac{1}{2}$	$44\frac{1}{2}$
10S	700	11	0	0	0
10S	700	41	7	Not taken	
10S	800	11	9	3	6
1FS	635	12.75	1	$\frac{1}{2}$	$\frac{1}{2}$
1FS	635	19.15	$2\frac{3}{4}$	$\frac{1}{4}$	$2\frac{1}{2}$
1FS	730	12.75	$1\frac{3}{4}$	0	$1\frac{3}{4}$
1FS	730	24.0	40	0	40
9FH	635	24.0	$1\frac{1}{2}$	1	$\frac{1}{2}$
9FH	725	24.0	$2\frac{1}{4}$	1	$1\frac{1}{4}$
9FH	725	30.35	$2\frac{3}{4}$	$1\frac{1}{4}$	$1\frac{1}{2}$
9FH	725	68.0	$3\frac{1}{2}$	$1\frac{3}{4}$	$1\frac{3}{4}$
9FH	725	74.35	Broke		

under the slow application of stress, while a shock may produce fracture. Considering the fact that in these tests permanent deformation took place within less than a minute after the application of the torque and also that there would be few practical cases where cooling would take place with sufficient rapidity to produce spalling within that time, it seems very probable that spalling would not occur at temperatures above that at which softening is apparent.

It is possible that the disintegration in some oil fired furnaces which has already been mentioned offers an exception to the statement just made. Oil flame temperatures are as a rule very high and the flame may either flutter or move about within the combustion chamber in a manner which is not characteristic of coal firing.

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[1] The weight as given was applied on the end of a 36-inch lever as shown in Fig. 14.

[2] One division on the scale corresponded to an angle of rotation of .0328 degree.

Since the radiation varies as the fourth power of the temperature, any change in intensity of the flame will be reflected immediately in the temperature of the wall and a thin layer on the inner surface of the refractory lining will be heated and cooled not only a large number of times, but with great rapidity. Although the temperature is ordinarily high enough that the refractory skin which is affected should be comparatively soft, the sudden changes may produce enough of a shock to cause cracking.

Since the temperature affects the true elasticity as well as the softening, a complete investigation on any one type of product should include elasticity measurements over the whole temperature range from room temperature up to the point of softening, as this will determine the range over which spalling is important. With these data and temperature graphs for a refractory wall or lining, it would also be possible to predict with a fair degree of accuracy the depth at which cracking would occur. However, time would not permit of enlarging the investigation to this extent.

In studying the figures given in Table VII, it should be kept in mind that it is the maximum elastic deformation regardless of the weight applied that is of importance in spalling. The amount of plastic deformation is, however, governed by the amount of stress.

Comparisons of the coarse and fine grinds are especially interesting. In addition to showing extreme differences in their elastic properties, the greater ease with which the coarse mixtures take on plastic deformation is also very evident. The elastic deformation was at a minimum on mixtures 1FS and 9FH, both of which were high in dense firing, plastic clay.

Discussion of Combined Data on Coefficient of Expansion, Elasticity and Rate of Temperature Change as Affecting Spalling

In order to check the results of the investigations which have been described, a number of the brick were spalled by heating one end at 1400°C for 15 minutes and then cooling in a blast of air for a like period. This was continued until each brick had lost 20% or more of its original weight. Three bricks of each kind, after being reheated at 1400°C for 5 hours, were also subjected to the regular water dip spalling test.[1] The latter test was made for general information and the results are not applicable to the other data obtained on brick which had not been reheated. All of these results are shown in Table VIII.

It is apparent that there are considerable differences between the lots tested. In the air spalling test the poorest results were obtained on the number 1 and 9 mixtures and the best on number 5 and 7. Mixtures 3, 6 and 7 also gave much better results on the coarse grinds than on the fine.

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[1] C38–21T, American Society for Testing Materials, p. 297. 1922 Tentative Standards.

Discussion From the standpoint of composition, the good results obtained on mixtures 3, 5 and 7 can be explained by the use of the "W" plastic clay. All of the other mixtures were bonded with the "K" plastic clay and reference to the curves showing

TABLE VIII

RESULTS OF SPALLING TESTS

Number	Water dip test (on reheated brick). No. of immersions causing failure. (Average of 3)	Air spalling test. (Brick heated at 1400°C and cooled in air). No. of coolings causing loss of 20% or more. (Average of 2)	Number	Water dip test (on reheated brick). No. of immersions causing failure. (Average of 3)	Air spalling test. (Brick heated at 1400°C and cooled in air). No. of coolings causing loss of 20% or more. (Average of 2)
1FS	2	$4^{1}/_{2}$	6FS	4	
1FH	2	1 (Only one brick tested)	6FH	3	$4^{1}/_{2}$
			6CS	5	
1CS	3		6CH	6	17
1CH	6		7FS	3	
2FS	5		7FH	3	$9^{1}/_{2}$
2FH	9		7CS	8	
2CS	10		7CH	10	28
2CH	11		8FS	5	
3FS	5		8FH	3	
3FH	6	$12^{1}/_{2}$	8CS	7	
3CS	10		8CH	8	
3CH	9	$18^{1}/_{2}$	9FS	1	
4FS	7		9FH	1	$2^{1}/_{2}$
4FH	6		9CS	2	
4CS	9		9CH	5	
4CH	12		10S	5	$11^{1}/_{2}$
5FS	13		10H	5	11
5FH	17	$30^{1}/_{2}$ (one brick broke from being dropped after 26th cooling)	11S	8	
			11H	6	
5CS	2				
5CH	4				

the porosities and firing shrinkages shows the former to be an exceedingly open firing clay with medium shrinkage and the latter to be of the dense firing variety. All of the flint clays used had approximately the same firing characteristics and on this basis it is not possible to make a distinction between the mixtures in which they were varied with the plastic clay remaining constant.

The rapid spalling of mixture 9 appears to be due to the replacement of 10% of the flint clay by a like amount of the dense-firing, calcined plastic clay.

Of the three factors, rate of temperature change, elasticity and coefficient of expansion, which affect spalling, the former apparently has no bearing on the spalling results obtained here, since there is no appreciable difference in this respect between the different mixtures, and this factor will, accordingly, be dropped from the discussion.

The coefficients of expansion and elasticity values, however, do vary considerably, the former to a much greater extent than was anticipated, although not nearly as radically as did the property of elasticity. However, the thermal expansion of mixtures 3, 5 and 7, which gave the best results in the air spalling test, are the highest of any of the mixtures tested, and, while the expansion is directly responsible for the stresses causing failure, its importance must be greatly overshadowed by that of elasticity. Although the elasticity values are somewhat masked by the softening effect and additional data should be obtained to show the relation more clearly, those which are given here are sufficient to prove that this property is the controlling factor in spalling and that it can be varied over wide limits.

Mixtures 1FS and 9FH, which failed rapidly in the spalling test and which had low thermal expansions, also had the smallest elastic deformation, while the 5FH and 7CH mixtures, which withstood the spalling test the best, and had relatively high thermal expansions, had the greatest elasticity, the difference between the good and poor spalling brick in this respect being in the order of 1 to 3 when measured at 725°C.

In general, all of the results of the elasticity tests paralleled those obtained in spalling, the major discrepancy being on mixture 3FH, which deflected the same amount as 9FH at 635°C, and yet gave materially better results in the spalling test. The particular sample which was tested may not have been representative of those which were spalled and for this reason it is unfortunate that there was not time for additional runs. The test being new, presented a number of difficulties which had to be overcome before progress could be made.

A comparison of the results shown for the fine and coarsely ground brick of mixture number 7 is striking. A ratio of 1 to 3 in the spalling test results was obtained and one of about the same order for elasticity. The coarsely ground brick also takes on a permanent set under a much lower stress than does the finely ground one.

This investigation was outlined several months ago and the most of the data accumulated before it was known that very similar work was being done at the Massachusetts Institute of Technology. The results which are given by Norton[1] lead him to the same general conclusion as that reached here, *i. e.*, that the elastic properties were by far the most important in determining the resistance to spalling. The coefficients of expansion given by him for some of the commercial fire clay brick are materially higher than any obtained in this investigation, but his values were for a maximum temperature of only 500°C, while those given here were for 800 and 1100°C, and it is possible that the particular specimens tested by him had larger coefficients of expansion over the low temperature range due to excess silica present. The values for elasticity which are given by Norton do not show as great differences between the various fire clay samples tested as are shown here, but this may be explained by the fact that his samples would, in all probability, not vary in structure to the extent that the ones in this investigation did. It is interesting to know that two such similar investigations as these can be conducted at the same time with fair agreement in the results and the same conclusion reached without knowledge by either laboratory of the other's work. It is unfortunate, however, that there should be such duplication of effort. A central clearing house such as has been suggested at different times for the promotion of efficiency in ceramic research would prevent such occurrences as this.

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[1] "A General Theory of Spalling," *Jour. Amer. Ceram. Soc.*, **8** [1], 29–39 (1925).

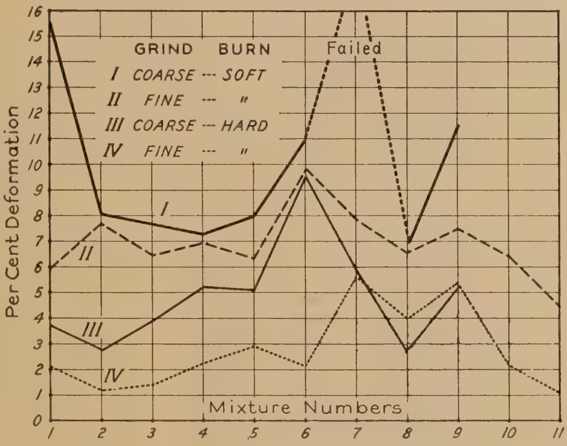

Fig. 15.—Deformation in standard load test. 1350°C—25 pounds/sq. in.

Deformation under Load

In order to determine the effect of grind and firing upon the deformation of fire clay brick samples of all of the mixtures used in the investigation on spalling were tested under a load of 25 pounds per square inch and at 1350°C, according to the standard method. The results are given in Table IX and shown graphically in Fig. 15.

The average deformation for the finely ground, hard fired brick is 2.76%, for the finely ground, soft fired 6.92%, for the coarsely ground, hard fired 4.97%, and for the coarsely ground, soft fired 9.44%.

From these averages and the detailed figures, it is evident that the degree of firing has a greater influence upon the deformation under load than is usually thought. The influence of grind is noticeable, but the firing produces a much greater effect, in fact it is of even more importance than the composition of the clays used. The latter statement would certainly not hold true with all clays, but it is only necessary to note the small amount of deformation obtained with the hard fired brick made entirely of plastic clay to realize that the degree of firing is of primary importance.

The differences in results obtained with the various mixtures are not sufficient to allow of any general statements in regard to the effect produced by varying the type of clay. The introduction of calcined flint clay in the place of uncalcined has little or no effect upon the amount of deformation under load, nor does its use reduce the difference between hard and soft fired samples.

TABLE IX

PERCENTAGE DEFORMATION IN THE STANDARD LOAD TEST AT 1350°C AND 25 POUNDS PER SQUARE INCH

Mixt.	Per cent deformation	Mixt.	Per cent deformation
1FS	5.92	6FS	9.86
1FH	2.11	6FH	2.13
1CS	15.50	6CS	10.90
1CH	3.78	6CH	9.66
2FS	7.71	7FS	7.86
2FH	1.19	7FH	5.63
2CS	8.10	7CS	Failed
2CH	2.80	7CH	5.95
3FS	6.49	8FS	6.57
3FH	1.41	8FH	4.00
3CS	7.68	8CS	6.75
3CH	3.94	8CH	2.76
4FS	6.96	9FS	7.50
4FH	2.29	9FH	5.39
4CS	7.27	9CS	11.57
4CH	5.30	9CH	5.42
5FS	6.35	10S	6.47
5FH	2.96	10H	2.18
5CS	7.98	11S	4.44
5CH	5.17	11H	1.11

Contrary to our expectations, the deformation of stiff mud brick was greater than that of soft mud products of similar composition. Only two comparisons are possible and the results in those cases are probably peculiar to the particular mixtures used. There was but little difference in grind and porosity between the soft and stiff mud brick which were tested and this partially accounts for the unexpected results.

Effect of Grind and Firing on Shrinkage

The figures which are given in Table X, showing the drying and firing shrinkage, were obtained at the plant where the test pieces were made and were supplied by S. M. Kier.

A study of these results reveals some points which should be of considerable interest to the manufacturer. The influence of grind on both drying and firing shrinkage is especially pronounced and indicates the necessity for accurate control in this part of the manufacturing operation when a product of uniform size is necessary. An average of all of the results gives the following:

	Shrinkage by volume		
	Drying	Firing	Total
Fine grind	11.8%	10.5%	21.0%
Coarse grind	7.3	5.9	12.8

The linear shrinkages would be approximately one-third of those given and the difference in total shrinkage would amount to almost $^1/_4$-inch on a length of 9 inches.

It may also be noted that in several cases the firing shrinkage of the soft fired brick is greater than that of the hard fired ones. This is largely due to the secondary expansion, which is discussed under the section on reheating, although it is also found here on the coarsely ground brick of the number 1 group, which are made entirely from plastic clay.

TABLE X

PER CENT VOLUME SHRINKAGE

Number	Drying, wet basis	Firing, dry basis	Total, wet basis	Number	Drying, wet basis	Firing, dry basis	Total, wet basis
1FH	17.1	12.6	26.4	6FH	12.8	11.2	22.6
1FS	17.1	13.0	27.9	6FS	12.8	13.1	24.3
1CH	11.3	2.8	13.8	6CH	9.3	0.8	10.0
1CS	11.3	12.0	21.9	6CS	9.3	5.3	14.1
2FH	12.7	14.8	25.6	7FH	13.3	10.0	22.0
2FS	12.7	13.4	24.4	7FS	13.3	10.7	22.6
2CH	6.0	6.9	12.5	7CH	10.5	0.2	10.7
2CS	6.0	13.0	18.2	7CS	10.5	4.8	14.8
3FH	10.9	14.5	23.8	8FH	9.8	1.5	11.2
3FS	10.9	13.9	23 2	8FS	9.8	1.2	10.9
3CH	8.0	8.0	15.3	8CH	4.5	1.5	5.8
3CS	8.0	10.6	17.7	8CS	4.5	1.1	5.6
4FH	11.7	14.8	24.7	9FH	9.4	6.7	15.5
4FS	11.7	12.5	22.7	9FS	9.4	3.5	12.6
4CH	7.2	10.7	17.1	9CH	3.7	4.0	7.7
4CS	7.2	8.2	14.9	9CS	3.7	2.2	5.9
5FH	9.0	13.1	20.9	10H	6.2	8.9	14.6
5FS	9.0	8.6	16.8	10S	6.2	13.0	18.3
5CH	5.6	8.3	13.5	11H	10.9	5.4	15.8
5CS	5.6	6.9	12.2	11S	10.9	11.5	21.1

Reheating Test The results obtained by reheating the various brick at 1400°C for 5 hours, which are given in Table XI, show the fallacy of using this test as a means of classifying fire clay brick according to quality.

It may be noted that when expansion takes place with both samples,

TABLE XI

LINEAR AND POROSITY CHANGES ON REHEATING AT 1400°C FOR FIVE HOURS

Number	Linear change	Apparent original porosity	Apparent porosity after reheating	Porosity change
1FS	1.26 expansion	15.2	15.0	0.2 decrease
1FH	0.42 expansion	4.8	5.0	0.2 increase
1CS	7.00 expansion	15.6	16.2	0.6 increase
1CH	1.39 expansion	11.3	10.8	0.5 decrease
2FS	0.21 contraction	22.3	19.6	2.7 decrease
2FH	0.24 contraction	19.4	20.0	0.6 increase
2CS	2.88 expansion	23.2	24.2	1.0 increase
2CH	0.54 expansion	21.6	19.3	2.3 decrease
3FS	1.14 expansion	26.5	26.3	0.2 decrease
3FH	0.43 expansion	23.4	23.1	0.3 decrease
3CS	2.27 expansion	26.1	28.5	2.4 increase
3CH	0.59 expansion	24.2	25.9	1.7 increase
4FS	0.33 contraction	27.0	20.5	6.5 decrease
4FH	0.19 contraction	21.5	19.4	2.1 decrease
4CS	0.93 expansion	24.1	16.3	7.8 decrease
4CH	0.84 expansion	19.4	16.1	3.3 decrease
5FS	0.69 contraction	26.5	24.5	2.0 decrease
5FH	0.12 expansion	25.8	24.6	1.2 decrease
5CS	2.19 expansion	25.9	21.5	4.4 decrease
5CH	1.37 expansion	25.7	....	....
6FS	0.35 expansion	22.3	17.5	4.8 decrease
6FH	0.29 contraction	15.0	13.8	1.2 decrease
6CS	2.48 expansion	20.0	....	....
6CH	0.60 expansion	16.7	15.2	1.5 decrease
7FS	0.51 expansion	25.6	19.1	6.5 decrease
7FH	0.40 expansion	20.0	18.4	1.6 decrease
7CS	2.11 expansion	25.1	21.3	3.8 decrease
7CH	0.48 expansion	20.7	....	....
8FS	0.17 contraction	23.4	23.2	0.2 decrease
8FH	0.01 expansion	22.5	22.4	0.1 decrease
8CS	1.70 expansion	17.9	19.2	1.3 increase
8CH	0.26 contraction	17.9	17.5	0.4 decrease
9FS	0.52 contraction	25.7	16.3	9.4 decrease
9FH	0	18.8	14.7	4.1 decrease
9CS	0.57 expansion	21.4	16.2	5.2 decrease
9CH	0.08 expansion	17.6	17.3	0.3 decrease
10S	2.04 expansion	17.8	13.9	3.9 decrease
10H	0.14 expansion	13.8	12.4	1.4 decrease
11S	1.35 contraction	19.7	16.8	2.9 decrease
11H	0.24 contraction	14.4	..	....

those which have been soft fired expand very much more than those which have been hard fired. At the time the reheating test was developed as a means of classifying brick, it was not recognized that expansion would take place to a marked degree from any other cause than over-firing with the accompanying softening and formation of a vesicular structure. It has since been found that with certain clays an expansion takes place with none of the evidences of over-firing and which is a function of the rate of original firing, as well as the temperature. This has been termed secondary expansion by Harvey,[1] who gives an interesting discussion of the subject.

The cause for this increase in volume is not known. It appears to be greater in amount under reducing conditions than under oxidizing and it is possible that it results from the evolution of oxygen by ferric oxide. That it is a function of the rate of heating is shown by the fact that brick may be fired in a slowly heated silica brick kiln and be of normal size, while if placed near the fire pocket in a fire clay brick kiln being fired only to cone 12, they will be very much over size.[2]

There is no definite relation between the linear and apparent porosity changes in the reheating test. In some cases a marked expansion is accompanied by a porosity increase and in others by a decrease. The true porosity would probably always increase with expansion as there does not appear to be a change in the specific gravity of the material.

This peculiarity of expansion without over-firing is found on clays from several districts, although it is much more pronounced on some of the flint clays from Pennsylvania than on clays from other localities.

This phenomena is of importance in determining the size of the brick fired according to the regular practice as is indicated in the section "Effect of Grind and Firing on Shrinkage" (p. 378).

In order to determine the effect of original firing conditions and rate of heating in the reheating test on the secondary expansion, a number of tests were conducted on brick of one brand made from Pennsylvania flint and plastic clays. In the results shown below the brick marked A were originally soft fired, but of normal size, those marked B were hard fired and normal size, and those marked C hard fired but oversize, while those marked D were soft fired and normal size, but from another lot than the A, B and C samples. The firing temperatures for the B and C lots did not vary greatly, the difference being largely in the rate of heating through placing in different positions in the kiln.

In the first reheat the brick were brought up to 1400°C in about 5 hours and held 5 hours; in the second 1400°C was reached in about 20 hours and the kiln held at that temperature for 5 hours; in the third the temperature was advanced to 1100°C in 3 hours and held there 1 hour; then advanced to 1200, 1300 and 1400°C at the rate of 100° in 30 minutes, the temperature being held at each of these points for one hour and 3 bricks drawn out at the end of each soaking period. In the fourth reheat the temperature was brought up to 1100°C in 5 hours and then advanced at the rate of 10°C per hour to 1400°C, three samples being drawn at each of the temperatures, 1250°C, 1300°C and 1400°C.

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[1] "Note on Secondary Expansion of Flint Clays," *Jour. Amer. Ceram. Soc.*, **7**, 455–6 (1924).

[2] From private notes.

The results obtained in these reheats are as follows:

Samples	First reheat (1400°C in 5 hours)
A	2.42% expansion (Average of 5)
B	0.20% expansion (Average of 5)
C	0.34% expansion (Average of 5)
	Second reheat (1400°C in 20 hours)
A	2.48% expansion (Average of 3)
B	0.31% expansion (Average of 3)
C	0.48% expansion (Average of 3)

	Third reheat (rapid rate)			
	1100°C	1200°C	1300°C	1400°C
D	0.06% con. (Av. of 3)	0.57% exp. (Av. of 3)	2.18% exp. (Av. of 3)	3.47% exp. (Av. of 3)

	Fourth reheat (10°C per hour from 1100°C)		
	1250°C	1300°C	1400°C
D	0.55% exp. (Av. of 3)	1.08% exp. (Av. of 3)	1.73% exp. (Av. of 3)

The first and second tests do not show appreciable differences in the expansions of the various brick. The third and fourth reheats, however, do show that the rate of heating is a governing factor in determining the amount of expansion and also that the expansion is a function of temperature within the limits of the tests. The rate used in the fourth reheat was as low as would be used in the majority of industrial furnaces during the initial heating up period and the expansion noted would take place in these furnaces unless it is lowered by the effect of the load which the brick supported.

Acknowledgment

The authors wish to give credit to H. F. Robertson, C. G. Denney and W. R. Kerr, all of whom coöperated extensively in obtaining many of the data given.

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THE DEVELOPMENT OF A CASTING BODY FOR VITRIFIED SANITARY WARE FROM AMERICAN MATERIALS[1]

By Andrew Foltz

ABSTRACT

This body casts in a very satisfactory manner. The time of two hours is entirely satisfactory when one considers that the molds were exceptionally dry. The pieces put through the bisque kiln came out without signs of warping or cracking. The appearance of the fired body was all that one could expect, considering that it was lawned through 60-mesh and was not magneted. With but slight modifications this body can be worked into our plant without any serious inconveniences.

The cost of the raw materials entering into the formula of Body No. 6 is about $3.00 per ton less than that of a similar body in which English clays are used. This is for the Trenton district.

The results of this work are given more to stimulate interest in the use of domestic materials than to give exact body formulas, it being realized that a formula developed for our peculiar conditions will not necessarily fit into another factory. It is to be hoped that other manufacturers will look into the possibilities of using our American clays.

Introduction

At the Annual Meeting last year we had a discussion on domestic and imported ball clays and kaolins. The result of this discussion left me with the feeling that everything was not quite what it should be with respect to the imported clays and, after mulling the thing over in my mind for a few months, I decided to try to develop a casting body from domestic clays. Other reasons which led to this decision were the facts that I knew that other potters were using some domestic clays in their mix, that one firm had for a number of years been using American clays almost entirely, and finally that I might show some saving in the cost of my raw materials.

Plan of Work Not being a technical man my scheme of investigation will probably not stand very close scrutiny; however, I wanted to get certain information and of course had to get it as any practical potter would. I decided to learn something of the casting characteristics of various clays that I thought worth considering. Of course I could not try them all, but I picked various ones that are more or less typical. I also decided to submit to the same tests some imported clays which were satisfactory for casting and some that were not, thinking that I might find out why these latter clays could not be made to work. With the results of tests on the individual clays as a guide, the plan was to take those that showed up the best and use them in developing a body.

Materials Used The clays used were in most cases obtained from users, while the feldspar and flint were from our own supply. The materials used and the companies selling them follow:

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, February, 1925. (White Ware Division.)

No. 12 English Ball	John S. Wright, Trenton, N. J.
Jernigan Ball (Tenn.)	H. C. Spinks Clay Co.
Old Mine No. 4 Ball (Ky.)	Ky. Construction & Improvement Co.
Whiteways English Ball	Hammil & Gillespie
J-P No. 11 Ball (Tenn.)	Johnson-Porter Clay Co.
Atlas Ball (Mo.)	R. T. Vanderbilt Co.
Hercules Ball (Mo.)	R. T. Vanderbilt Co.
Klondyke Kaolin (Ga.)	Edgar Brothers Co.
Cherokee Kaolin (Ga.)	R. T. Vanderbilt Co.
Lake County Kaolin (Fla.)	Lake County Clay Co.
Edgar Plastic Kaolin (Fla.)	Edgar Plastic Kaolin Co.
Harris Kaolin (N. C.)	Harris Clay Mining Co.
A-1 China	Hammil & Gillespie
M. W. M. China	Moore & Munger
Peerless Kaolin (S. C.)	R. T. Vanderbilt Co.
Feldspar	Eureka Flint and Spar Co.
Feldspar	Genessee Feldspar Co.
Flint	Eureka Flint and Spar Co.

Procedure The tests on the individual clays consisted in making up 5000 gram batches according to the following formula:

$$\left.\begin{array}{l}\text{Clay } 50\%\\ \text{Feldspar } 25\%\\ \text{Flint } 25\%\end{array}\right\}\ \text{All weights calculated on dry basis}$$

These mixtures were blunged in regular bucket agitators with a sufficient quantity of water to make a workable slip and alkali solution made according to the following formula was added from time to time until maximum deflocculation was reached. At this point a small quantity of reserve body was added to bring the slip to a point where settling of the flint and feldspar would not occur; the slip was then lawned through a 60-mesh standard screen, the specific gravity determined and the mixture cast in molds as described later.

The alkali solution used was made up so that each 10 cc. of solution contained 0.5 gram of water glass and 0.5 gram of dehydrated soda ash. The water glass had a specific gravity of 1.36.

Viscosity tests were made with a flow type viscosimeter having a $^5/_{32}$-inch orifice.[1]

The test piece used throughout the preliminary casting tests was designed so that it could be cast by what is termed "solid casting," that is, a core was used. The piece was approximately 4 inches square and $3^3/_4$ inches high and the walls were about $^{11}/_{16}$ inch in thickness, the bottom being slightly thinner. The pour holes were all reamed to the same size, *viz.*, $^{15}/_{16}$ inch. All molds were made from the same case. The slip entered at what would be the bottom of the piece, that is, the pieces were cast upside down.

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[1] See *Trans. Amer. Ceram. Soc.*, **17,** 331 (1915).

In order to determine the relative speeds of casting for the various clays a glass probe was introduced through the funnel at various times and the time noted when the $^{15}/_{16}$-inch opening had entirely closed. The molds were then opened and the pieces were taken out, sponged, dried and fired to cone 9.

The data obtained and observations taken on the clay bodies were:

1. Water added in cc.
2. Standard alkali solution added in cc. for maximum deflocculation.
3. Deflocculation curves for all bodies.
4. Viscosity at maximum deflocculation.
5. Specific gravity at time of casting.
6. Time for shut-off.
7. Character of cast.

An attempt was made to cast all of the mixtures at the same specific gravity, but it was soon found that this was impossible due to the nature of the clays used. It was then decided to use as high a specific gravity as could be maintained and still get a slip that would flow from the viscosimeter. This was accomplished by adding the dry body bit by bit to a definite quantity of water in the blunger, noting how the water "took" the mixture and adding more water as seemed necessary to bring about the desired result. In most cases a quantity of the alkali solution was also added with the water used for adjusting. When the body was thoroughly blunged, additional alkali solution was added until the slip would flow 100 cc. from the viscosimeter without cutting off due to thickening. Alkali solution was then added, 20 cc. at a time, the body blunged 15 minutes after each addition and the viscosity tested for each addition. In the case of clays which were sluggish in their reaction to the alkali the blunging was increased to 30 minutes. The viscosity curves shown all start with the alkali addition at which a sustained flow for 100 cc. could be obtained with the viscosimeter used.

The data obtained and the viscosity curves for the various bodies follow. The numerals shown over each curve represent the specific gravity of the slip when cast; the gravity at maximum deflocculation being approximately 0.01 less in each case.

Discussion of Preliminary Tests

No. 12 English Ball This is a dark-colored clay containing a considerable quantity of lignite. The clay reacts very quickly to alkali and has good flowing qualities. In time required for casting this clay stood highest of all the clays studied. The cast piece was solid and released well from the core even after being in contact with the plaster for 12 hours.

Jernigan Ball This is a dark colored Tennessee clay. Contains some lignite. Has good fluidity and reacts quickly to alkali. Of the dark colored ball clays investigated this clay casts the quickest, the time required being 4 hours. The test piece was solid.

Old Mine No. 4 A dark colored Kentucky clay. Has good flowing qualities and reacts very quickly to alkali. Contains lignite. In speed of casting it comes next to No. 12 English ball. Casts solid.

Whiteways English Ball A clay somewhat lighter in color than some on the market. Much more fluid than No. 12 but reacts about the same to alkali. Contains small amount of lignite. Casts good and solid.

J-P No. 11 Ball A light colored Tennessee ball clay. Very sluggish in its reaction to alkali. Flowing qualities not very good for a ball clay. Requires an excessive amount of water to work properly. Casts in $2^1/_2$ hours, being the fastest of the true ball clays. Has tendency toward "livering." Requires more alkali than any other ball clay studied. Casts good and solid.

Atlas Ball Clay An exceedingly dark colored clay from Missouri. Contains some lignite. Very good flowing qualities and does not require much alkali for deflocculation. Reacts quickly to alkali additions. Casts good and solid in $4^1/_2$ hours.

Hercules Ball Clay Another Missouri clay containing considerable lignite. Reacts very quickly to alkali and requires the lowest amount for deflocculation. Flows well even at high specific gravity. Casts good in 8 hours' time.

Klondyke Kaolin A washed Georgia clay. Reacts fairly quickly to alkali and has good fluidity for a kaolin. Casts good and solid in 25 minutes.

Cherokee Kaolin Another washed Georgia kaolin. Slightly more sluggish in its reaction to alkali than Klondyke. Has a very long flowing range and good flowing qualities although rather slow. Casts solid in 30 minutes.

Lake County Kaolin A washed Florida clay. Very sluggish in its reaction toward alkali. Has very pronounced tendency toward "livering" and requires considerable water to make a workable slip. Requires a large amount of alkali for deflocculation and has a short flowing range within the gravity used. Casts good in $2^1/_2$ hours.

Edgar Plastic Kaolin Another washed Florida clay. Practically the same in its action as Lake County Clay but casts somewhat faster, taking but 2 hours.

Harris Kaolin A washed North Carolina clay. Very coarse-grained and contains some mica. Very sluggish in its action toward alkali and "livers" readily. No viscosity test could be made due to this "livering" tendency and conditions governing the preparation of the slip for casting had to be gaged by more or less rule-of-thumb methods. The slip shut off in 5 minutes and the results of the test were exceedingly poor, the piece being hollow and it cracked in the mold.

A-1 China A washed English clay. Reacts quite rapidly to alkali additions. Does not have good flowing qualities. Casts exceedingly well making a solid piece in 5 minutes.

M. W. M. China Another washed English clay, very fine grained. Very sluggish in its action toward the addition of alkali. "Livers" very rapidly. Gave no viscosity range within the specific gravity limits covered. Casts slightly hollow in about 12 minutes.

Peerless Kaolin A crude South Carolina clay. Reacts about the same as the Georgia kaolins toward alkali. Has good flowing qualities. Casts good and solid in about 15 minutes.

Discussion of Deflocculation Curves

The curves in Fig. 1 show the point of alkali addition at which the slips would first give a maintained flow of 100 cc. without thickening. They also show the alkali additions necessary for complete deflocculation. It will be noted from the numerals over each curve, which represent the specific gravity at maximum deflocculation, that this characteristic was not constant. If all gravities had been brought to that of the lowest recorded, namely Lake County kaolin at 1.62, the effect would be to lower all curves toward the base line and to increase the distance between the point of maximum deflocculation and the point at which sustained flow began.

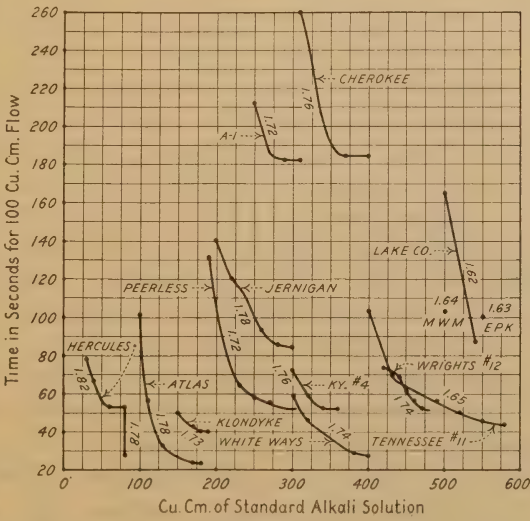

FIG. 1.

This of course would have no effect on the amount of alkali necessary for complete deflocculation.

It will be noted that the clays roughly group themselves into three groups, *viz.*, those requiring less than 200 cc. of alkali solution, those requiring between 200 cc. and 400 cc. of solution, and those requiring over 400 cc. for complete deflocculation. No definite relation can be noted between the amount of alkali required for deflocculation and the action of the clays in casting. Most of the clays, however, that required over 400 cc. for deflocculation were very sluggish in their reaction to the addition of alkali.

Study of Combinations of Clays

With the results of the tests on the individual clays at hand, two questions at once came up. These were: (1) Will a slow-casting ball clay in combination with a kaolin cast more slowly than a quick-casting ball clay in combination with the same kaolin, and (2) will the amount of alkali necessary for complete deflocculation of two clays in combination be equal to the sum of the percentages of the individual clays times the amount of alkali necessary to deflocculate each clay? For this test Old Mine No. 4 ball clay, Hercules ball clay, and E. P. K. kaolin were used.

The combinations used were as follows:

	No. 1 body	No. 2 body	Alkali required, cc.	Time for casting, hrs.
Old Mine No. 4	25	..	360	11
Hercules	..	25	80	8
E. P. K.	25	25	550	2
Feldspar	25	25	...	..
Flint	25	25	...	..
Body No. 1	..	..	440	$2^3/_4$
Body No. 2	..	..	120	4

This test shows that the combination of an 8-hour clay with a two-hour clay casts more slowly than a combination of an 11-hour clay and the same 2-hour clay. Furthermore, while body No. 1 would indicate the answer to question No. 2 to be in the affirmative, body No. 2 shows that the relation does not always hold. Another combination of clays put through the same test gave the same result. The conclusions drawn from these tests were: (1) in casting slips, clays in combination lose to some extent the characteristics they exhibit individually and while results of tests on individual clays are of great aid, one cannot use them as an absolute guide in compounding body mixtures, so that (2) the development of a casting body must be studied from the standpoint of combination of clays.

Study of Casting Bodies

There were three primary conditions that must be met in developing a casting body for our plant: first, it must mature at cone 9; second, it must be suited for "solid casting;" and third, it must "cast up" in not more than $2^1/_2$ hours. Other considerations which probably apply to all sanitary ware casting are: (1) it must "stick up" readily; (2) it must have good flowing qualities; (3) it must release easily from the cores; (4) it must have a dry strength sufficient to withstand ordinary handling; (5) it must sponge smoothly; (6) it must have a good fired color; and (7) it must not warp during firing, nor dunt. Another quality which, though desirable, is not entirely essential is that the body should show a maximum deflocculation with an alkali addition of not over $^4/_{10}\%$ of a half and half mixture of dehydrated soda ash and water glass having a specific gravity of 1.40.

From the results of the casting tests on the individual clays and from other physical data as noted, it was decided that the following clays would be tried in the body development.

Lake County Kaolin	Color, strength
Peerless Kaolin	Flowing quality, cost
Harris Kaolin	Color, open texture.
Old Mine No. 4 Ball	Color, flowing qualities
Jernigan Ball	Fast casting
Hercules Ball	Color, flowing qualities, low alkali

Three body mixtures were made as follows in order to study the action of these clays in combination. The batches were 10,000 grams each and the method of preparation and casting was the same as that described for the individual clays.

	No. 3	No. 4	No. 5
Feldspar	20	23	25
Flint	30	32	30
Lake County	10	8	6
Peerless	16	8	8
Hercules	6	6	8
Old Mine No. 1	18	6	18
Jernigan	..	12	..
Harris	..	5	5

The results of these tests were:

	Cc. alk. solution	Min. viscosity	Sp. gr.	Time for shut-off
No. 3 body	370	80 sec.	1.85	$3^1/_4$ hrs.
No. 4 body	350	92 sec.	1.85	2 hrs.
No. 5 body	320	93 sec.	1.84	$2^3/_4$ hrs.

With the results of the tests on the above mixtures as a guide, it was decided to make up the next body on a semi-factory scale and cast a large tank and cover. We have a miniature slip house equipment in our laboratory and we have used this enough to know that when results are satisfactory from this equipment, only slight adjustments are necessary to put a body directly in the factory. The machine handles 100 lbs. of dry material per batch.

The batch for the semi-factory test was:

Body No. 6

Genessee Feldspar	35
Eureka Flint	25
Lake Co. Kaolin	5
Peerless Kaolin	7
Harris Kaolin	5
Hercules Ball	6
Old Mine No. 4	17

This body tested out as follows:

Alkali solution used	1700 cc.
Alkali solution necessary for complete deflocculation	1800 cc.
Specific gravity when cast ($30^2/_3$ oz. per pt.)	1.84
Time for 100 cc. flow at sp. gr. of 1.84 and 1700 cc. alkali addition	86 sec.
Time required to cast	2 hrs.

Clay	H_2O added in cc.	Cc. of standard alkali solution	Viscosity	Wt. per 100 cc.	Character of cast	Time for shut-off
English No. 12	1950	480	52″	174	good	12 hrs.
Jernigan Tenn.	1900	300	83″	178	good	4 hrs.
Kentucky No. 4	2000	360	51″	176	good	11 hrs.
Eng. Whiteways	1900	400	28″	174	good	10 hrs.
Tenn. No. 11—J.P.	2750	580	43″	165	good	$2^1/_2$ hrs.
Atlas	2100	180	24″	178	good	$4^1/_2$ hrs.
Hercules	2150	80	28″	178	good	8 hrs.
Klondyke	2300	190	42″	173	good	25 min.
Cherokee	1900	400	194″	176	good	30 min.
Lake	2950	540	87″	162	good	$2^1/_2$ hrs.
E. P. K.	3400	550	100″	163		2 hrs.
Harris	2680	335	...	167	hollow n. g. cracked	5 min.
A1	2300	260	237″	172	good	5 min.
M. W. M.	2750	520	128″	164	fair	12 min.
Peerless	2250	310	51″	172	good	15 min.
Body No. 1	2120	440	123″	181	good	$2^3/_4$ hrs.
Body No. 2	2080	120	93″	185	good	4 hrs.
Body No. 3	....	370	80″	185		$3^1/_4$ hrs.
Body No. 4	....	350	92″	185		2 hrs.
Body No. 5	....	320	93″	184		$2^3/_4$ hrs.
Body No. 6		1700	86″	184		

LAMBERTVILLE, N. J.

RAPID CHECK-TESTING FOR FELDSPAR FOR USE IN VITRIFIED FLOOR TILE[1]

BY NUGENT A. RAGLAND

ABSTRACT

A simple laboratory test is described wherein successive shipments of feldspar are checked against preceding shipments. This method gives a very accurate idea of variation of feldspar shipments. It outlines a method whereby corrections for relative fluxing values may be made and at the same time body control can be maintained direct from the shop laboratory insuring consistent firing practice from month to month.

Many tests for feldspar have been submitted for approval which include fusion buttons, cones, flow trials, chemical analyses, etc. Chemical analyses have been more or less popular but due to the fact that the average layman does not reckon his feldspar in terms of "ideal feldspar," we have submitted a test now carried out at the Perth Amboy Tile Works which has given us satisfaction and has been adopted as standard practice for body control. It also gives us an idea of the "fluxing value" of successive cars of feldspar checked against a standard.

All tests are carried out on the dry basis, percentage being taken as such. Therefore, it is necessary to determine the batch weights of the standard body upon the dry weights.

When a car of feldspar arrives, it is sampled by collecting approximately fifty pounds from various parts of the car. This is piled and quartered rejecting opposite quarters, and the same process repeated a second time.

The remainder is placed in a laboratory oven and thoroughly dried over a hot plate or in a drier at 212°F.

The following procedure is followed using at all times moisture-free ingredients. The standard body is composed of 60% feldspar, 5% flint, and 35% clay. At the above figure the feldspar is assumed correct for the present firing temperature. When a shipment of feldspar arrives it is sampled, and the following bodies are made up holding the clay content constant at 35%. The difference of feldspar is made up with flint.

Body	No. 1	No. 2	No. 3	No. 4	No. 5
Feldspar	56	58	60	62	64
Flint	9	7	5	3	1
Clay	35	35	35	35	35

This procedure is carried out because the impurity in feldspar is usually flint and occasionally a small amount of clay which is negligible.

The trials of these bodies are pressed and also the trials of the standard body or commercial body then in use. Some trials are set out for check against the following car. It is necessary that the moisture content of the

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[1] Recd. Jan. 27, 1925. Presented at the Annual Meeting of the AMERICAN CERAMIC SOCIETY, Columbus, Ohio, Feb., 1925. (White Ware Division.)

dust is constant in each body and that the pressure applied to the trials is the same in all cases. These trials are fired with like body trials face to face in the extreme and easy part of the kiln, *viz.*, one sagger directly over the bag wall and one sagger in the center at the floor of the kiln. The bodies should be set together carefully packed in sand, and cone pats should be placed in each sagger.

The fired trials are compared for shrinkage and the ink test is used upon each trial. Use the new shipment of feldspar between the limits of where it takes ink in the fourth ring and where it sticks to the other trials (or blisters) in the first ring keeping toward the limit of the ink test in the fourth ring. Of course, firing must be even and constant in all cases.

When the next shipment arrives it is made up and checked in the same manner against the former shipment using the ink test and observing blistering and sticking limits.

If the shrinkage of the proper body is too high or too low, it may be overcome by addition or subtraction of clay at the expense of flint.

In commercial practice we fire a good cone 11 down and attempt to soak this cone down in all parts of the kiln. Naturally the desirable feldspar for our use, then, is one which shows a fairly low vitrification and a high overfiring temperature.

This method, while very simple, gives us:

(1) Uniformity of firing conditions (or temperature) from kiln to kiln, eliminating guess work and hazard and enables the fireman to fire successive kilns alike thereby acquiring better efficiency.

(2) Idea of fluxing values of successive shipments of feldspar.

(3) Complete body control from laboratory, any errors occurring being mechanical or firing defects.

PERTH AMBOY TILE WORKS
PERTH AMBOY, N. J.

POTS AND PINES, A DECORATIVE PROBLEM FOR THE ARTIST POTTER[1]

BY MARGARET K. CABLE

ABSTRACT

A descriptive article outlining the method of producing a soft green pine tree decoration for vases and pots.

Introduction

My vacations are spent among the pines of northern Minnesota. I drink them in all summer, I long for them all winter, and being a potter they naturally have formed the "theme" of many a pot.

It is my purpose to outline here the method followed in the production of the soft green pine tree vase shown in the accompanying photograph. This type of decoration and this particular spruce-green color effect has been reproduced many times by my advanced students in ceramics, which fact together with the photograph should prove that the process is a practical one.

Body A light-colored cream or buff body is essential if the semi-transparent matt glaze given below is employed. Entirely different color effects would be produced were a red or dark firing clay used.

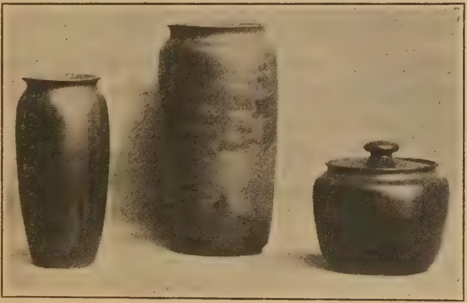

FIG. 1.

Shaping the Ware The pieces may be hand-built, thrown or cast, at the convenience of the worker, but a smooth even finish upon which to paint the pattern is needed. The form and size should be suited to the pine tree design.

Drawing in the Design After the wet clay piece has been fashioned and finished down quite smooth, allow it to dry out completely to the dry "green" stage. The form is now ready to decorate. The pine tree pattern may be traced or drawn free hand on the dry clay pot with a pencil or brush.

Painting in the Color Place about a gram of copper carbonate on a ground glass slab and add two or three drops of dissolved gum arabic and enough water to make a thin paste. Grind with a palette knife until thoroughly mixed and perfectly smooth. Thin out with water to a consistency which will flow easily from the brush. Select a large soft water-color brush and apply the color to the pattern in a very thin even coat. Care must be taken to get the copper wash very thin and as even as possible for, if put on too heavy or lumpy, the copper will develop in the kiln uneven dark and metallic spots in the glaze. The decorated ware should then be biscuited to cone 05 or 06.

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[1] Presented at the Annual Meeting, AMERICAN CERAMIC SOCIETY, February, 1925. (Art Division.)

The Glaze

The biscuit piece is then glazed with a thin coating of one of the glazes given in the table below, depending upon the color desired. If a dark green pine tree is to blend into a lighter green background the green glaze should be used. Or a green and blue color combination may be achieved by using the blue glaze, in which case the pine trees will show up green against the blue background.

If, however, a brown glaze is to be applied the pattern painted in copper will come through in a darker shade of brown. Some very pleasing effects are obtained by painting a design of bare trees upon the pot, the interlacing branches of which form a semi-conventional border about the top, while the upright trunks serve as a pleasing perpendicular breaking of the background space. A brown glaze shading off into a tan yellow applied over this pattern gives the effect of naked trees against a soft hazy sunset sky.

CHEMICAL FORMULA OF GLAZE

$$\left.\begin{array}{ll} PbO & 0.476 \\ CaO & .430 \\ K_2O & .094 \end{array}\right\} \; Al_2O_3\,0.378 \left\{ \; SiO_2\,1.13 \right.$$

Batch Weights

Grind in a ball mill for $1^1/_2$ hours. Screen through 100-mesh screen. Add 1 teaspoon dissolved gum arabic before screening.

	Green	Blue	Brown	Yellow
White lead	200	200	200	200
Whiting	70	70	70	70
Feldspar	85	85	85	85
Kaolin	120	120	120	120
Black oxide copper	7			
Black oxide iron	3			
Black oxide manganese	1.5			
	486.5			
Black oxide cobalt		1.5		
Black oxide nickel		1		
		476.5		
Black oxide manganese			6	
Black oxide iron			13	
			494	
Black oxide managese				3
Black oxide iron				6.5
				484.5

Application of Glaze The above body glaze is of the stationary type, that is, it remains exactly where it is put provided it is not put on too heavy or much overfired. When applied in a medium thin coat and fired at the temperature indicated, it comes from the kiln a soft, silky, semi-transparent matt.

This glaze does not, however, correct any defects of application and must, therefore, be applied with great care. The ideal method, when dealing with a glaze of this kind, is to spray it on with compressed air, but if this is not available it can be either poured over the pot or the piece dipped in a bath of glaze. In either case the finger marks must be retouched very carefully and all drips or uneven places scraped down to prevent their showing in the finished work.

The Fire The glazed pots should be handled as little as possible and placed in the kiln with care as the scratch of a finger nail or the least chipping or marring of the unfired glaze will disfigure the fired ware. Firing should be carried to cone 1 in an ordinary oil-burning muffle kiln of the usual type.

Caution To be on the safe side, it is better to have the copper wash a little thin rather than a bit too thick.

The same may be said with reference to the application of the glaze. It will not turn bright or glossy if applied thin, as many other matt glazes have an unpleasant habit of doing. Therefore, put it on evenly but not too generously. Remember that a thinly glazed piece can, if necessary, be reglazed and refired, but a pot with a thick heavy coat of glaze, which obliterates the decoration beneath, is a lost pot and like the luckless pot of Omar, which was marred in the making, may find itself consigned to a warmer place than the kiln, which would be a sad end for a cool breezy pine tree pot.

University of North Dakota
Grand Forks

KILN STOKERS[1]

By John D. Martin

ABSTRACT

This paper presents the industrial application of kiln stokers, a description of which has been previously given.

During the last year we have been operating a kiln firing refractories equipped with these stokers. It is a round down-draft kiln and we have fired it about once every six weeks. During this time we have been running what might be called a continuous test of the stokers from a mechanical standpoint to develop and correct such weaknesses which would become evident from wear, breakage, warpage and burning out of some of the parts.

An experience of twenty-five years with machinery has shown me that because a machine when new will start working quite well, it does not always follow that it can be considered a finished product. Although the theory of the machine may be well founded, its performance may eventually be unsatisfactory on account of faulty design, the poor choice of materials of construction resulting in excessive wear or breakage or both.

As to the general theory of our stoker the rotating round grate which we employ was first used in England over one hundred years ago, while an auger feed and the underfeed principle which we use are both very old in the art of combustion. However, certain of our claims of improvements over past forms of such stokers have been allowed by the United States Patent Office.

I do not contend that some sort of properly designed overfeed or chain grate stoker cannot secure results in firing clayware, but this will be a much more complicated machine than ours when worked out to use forced draft, which should be utilized by all means. One of our chief aims has been to avoid a complicated machine that a fireman of average intelligence could neither understand nor operate.

Our stoker consists of a horizontal feed pipe placed below the grate level and this extends from a coal hopper on the outside of the kiln to a point underneath the center of a round grate where it is attached to the specially constructed feed pipe ell. Extending upward from this ell is a vertical feed pipe which conveys the coal upward toward the center of the grate by means of a vertical auger in the same manner as the coal is conveyed from the outside hopper to the ell by the horizontal auger operating in the horizontal feed pipe. Power is applied to turn the horizontal auger at its outer end of course, and also to drive a shaft which extends back underneath the horizontal feed pipe into the bottom compartment of the ell where by means of a pair of miter gears we impart rotation to the vertical auger. This is done by means of a short vertical shaft which extends upward from one of these miter gears into a square hole in the central core of this auger.

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb., 1925. (Heavy Clay Products Division.) Other presentations of the subject by Mr. Martin have been published. See *Jour. Amer. Ceram. Soc.*, **6** [10], 1044 (1923); *ibid.*, **7** [12], 887–888 (1924).

The frame which supports the grate has a central sleeve which fits over the vertical feed pipe and rests on the top of the ell which acts as the bearing. The frame is thus supported by the top of the ell and the vertical feed pipe and is free to rotate. The ell itself is held in place by a large ring set in the brickwork of the kiln having spokes extending inward toward the ell. They end in another ring which encircles the ell and supports it.

The sleeve spoken of above which fits over the vertical pipe has spokes extending outward and these carry the grate at their outer ends. The outside edge of the grate lies over the edge of the large ring set in the brickwork, and this grate as a whole is approximately cone shaped. It is composed of a series of flat rings placed one over the other and each one is smaller in diameter than the one below. Combustion air enters the fuel bed in a horizontal direction between these rings. They are made wide enough so that the siftings cannot normally fall off their inside edge into the windbox which of course is the compartment immediately underneath the grate.

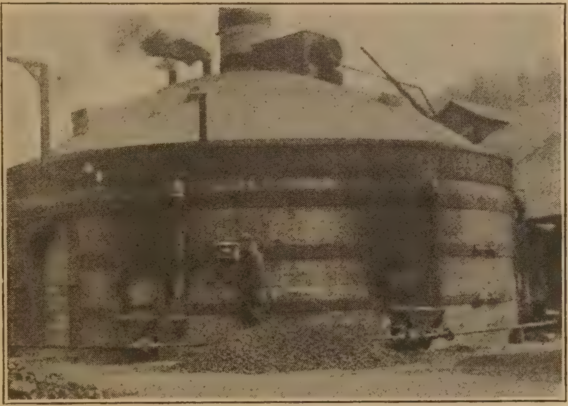

FIG. 1.—Refractories kiln, stoker fired.

Coal entering on the grate through its center at the top of the cone gradually works its way down over the grate to its outside edge where it can be scraped off as ash as the grate revolves. This ash falls outside of the windbox into the bottom of the passageway in the kiln wall made as part of the stoker layout. The bag wall of the furnace will be a half circle set around the inside half of the grate. The other half of the grate should be under the kiln wall arch.

The stokers are all driven from one point by means of shafting equipped with universal joints to enable it to go around the kiln from one stoker to another. This shafting is on a level with the center of the horizontal feed pipe and would generally be about a foot off the ground.

Forced draft is introduced from one side of the windbox just underneath the outside edge of the grate. It cannot be interfered with by any accumulation of siftings under the grate because a way is provided to automatically discharge them by means of the rotation of the grate together with a small spiral wrapped around the horizontal miter gear shaft from the ell to the outside of the wind box. Thus this shaft also acts as a conveyor to discharge siftings from the windbox.

One of the most troublesome things for us to solve has been to find the best means to rotate the grate. We started by using shafts and gears but the expansion and slight warpage of these parts under heat resulted in so much trouble we gave these up. But this experience taught us always thereafter to see the necessity of providing ways and means of handling expansion and warpage which cannot be avoided in such a way as to keep us out of trouble. We next put a chain sprocket around the bottom of the central grate frame sleeve and for about two years rotated the grate with a chain and during this period we increased the size of the chain three times. The shaft of the driving sprocket is driven by a pair of worm gears, the worm being located on the horizontal miter gear shaft underneath the horizontal feed pipe. We have recently found, however, that we can simplify the construction by the use of a ratchet drive having fewer and less expensive parts. A recent test has shown very gratifying results. We fired this stoker for a week with the kiln empty but we closed in the bag wall on top to make the furnace very hot. During this time the stoker developed no mechanical trouble whatever. We finally decided to see if we could not stall the grate so the hot bag wall was deliberately tipped over and allowed to fall onto the grate. But apparently even more drastic means than this would have to be employed as this neither stalled the grate nor injured it. It carried this load and kept on revolving just the same.

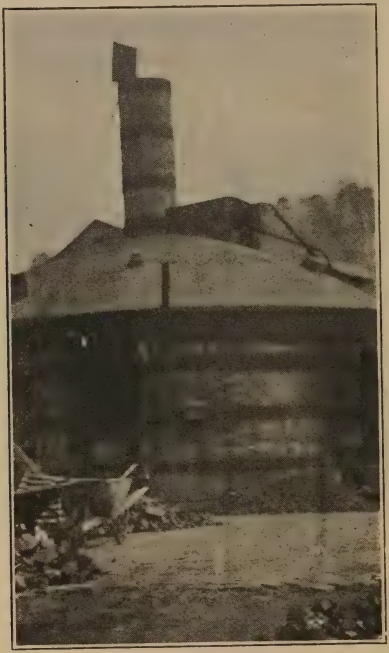

FIG. 2.—Kiln on high fire, notice absence of smoke.

Our experience with the means of rotating the grate is typical of the development of most of the stoker. Our aim has not been to let any part of the stoker get by in just a fashion but to find and use the best means we can evolve. One of these stokers in operation seems to be quite a simple affair but it has been no simple matter to develop it so because literally every square inch of it has been gone over time and again to fit it to stand the heat strains of expansion and contraction, the crowding of the furnace walls against it, the very great difficulty of furnishing any proper lubrication to some of the parts and to protect it against the presence of tramp iron in the coal. We have tried many ideas which were dismal failures, but so far we have not met a problem which we have not eventually been able to solve; but a detailed story of all the different devices and schemes which have been tried out and most all of which have been discarded, in order at first to make the stoker work at all, and finally to simplify it and make it perform better and better, would fill a volume as we have now spent over four years and thousands of dollars on the problem.

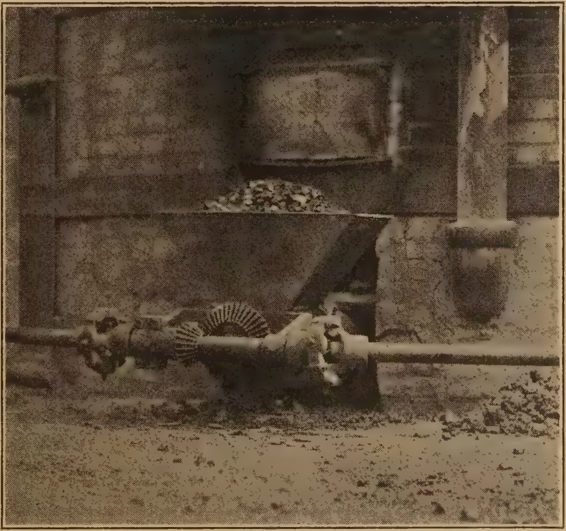

Fig. 3.—Stoker in position showing shaft drive.

Some of our difficulties have not shown up with certain features until they have been in operation for as long as a year. About four months ago, for instance, the vertical augers in one after the other of the stokers commenced to run very hard and some of them stuck and would not move at all. We found the trouble was in the lower compartment of the feed pipe ell where the miter gears are located. The miter gear on the short vertical shaft which operates the vertical auger had been placed so that its teeth were on top. This shaft has a bearing where it goes through the wall which separates the lower and upper compartments of the ell. After this bearing wears, fine coal dust will come down through it and fill the lower compartment sufficiently to clog the teeth of the miter gears and prevent them from operating. We first tried stopping this condition by using a bushing for a bearing through this wall. The bushing was screwed into the wall and extended upward into the central core of the vertical auger. We thought no fine coal dust would find its way upward over the top of this bushing and thence down into the lower compartment. After the dust rose about two inches along the outside of this bushing, there being a clearance between it and the auger of $^1/_{16}$ inch, and before it reached the top of the bushing, it became so packed that it froze the auger tight and we gave up that plan. We have now installed a hard brass bushing which can be quickly renewed after it wears enough to let dust through and have inverted the miter gear to the top of the compartment to keep it out of any dust for a much longer period and have also provided a way of quickly cleaning out this compartment while the stoker is in operation.

If the fuel bed is kept thin so that it will tail out at the edge of the grate, there will be no trouble with clinker formation on the furnace walls. Of course if a coal is used which has a very high fusion point of the ash there will be no clinker on the wall even if the fuel bed is thick enough to extend upward on it. This has been our experience with a certain grade of W. Va. coal which has a fusion temperature of the ash of 2800°. We have experimented with an air cooled furnace zone extending upward about six inches above the level of the edge of the grate. This zone was made of hollow refractory blocks with air circulated through them, and it did the work. In this connection it may be interesting to note that we had no trouble at all in freezing one of the biggest clinkers we ever saw onto a lining made up of a well-advertised "clinkerless" material composed largely of carborundum and these nine-inch brick cost us something over a dollar each. Fortunately, however, we had only indulged in about thirty of them for a trial.

The fact that we have already spent four years on this stoker will no doubt raise the question in the minds of some as to the probability of our working on a problem which we cannot solve, but it must be understood that the process of testing out any device in actual service which requires many changes, is of necessity a long drawn out one if the testing has to be carried on intermittently as on a periodical kiln which can be fired only once in three weeks. Further delay is also experienced by the time required to make drawings of changes contemplated, having new patterns made for castings, machining and installing them. No doubt we would seem to have progressed faster if we had confined our work to one test stoker, but we have believed that the better way would be to put these stokers to work right under actual firing conditions which we are sure could not be duplicated in any test installation. They are being raised on a diet of hard knocks received in actual service firing clayware, and when they have grown up properly, we will put about four hundred of them to working for us at our plants and will offer them to our industry as a proven means to secure economical firing.

Straitsville Impervious Brick Co.
New Straitsville, Ohio

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ORIGINAL PAPERS

AN X-RAY STUDY OF NATURAL AND ARTIFICIAL SILLIMANITE

By John T. Norton[1]

ABSTRACT

Mechanical mixtures of alumina and silica in the molecular proportions of 1:1 and 3:2 as well as samples of pure kaolin, have been heated to temperatures above 1500°C and have been examined by the X-ray diffraction method. The diffraction patterns obtained from these samples agree exactly with the pattern given by a sample of natural sillimanite, not only in the position of the diffraction lines but in their relative intensities. This indicates that the regularly arranged atoms of these two compounds must have identical positions. It is concluded that either the two compounds are identical or that each unit of the lattice of one compound contains a definite number of randomly arranged atoms which the other compound does not possess.

The mineral sillimanite which occurs in nature is quite well known and, as a result of many analyses, is believed to be a compound of alumina and silica in equal molecular proportions. There has also been found in fire clay and porcelain articles which have been heated, particularly for long periods at temperatures above 1500°C, a crystalline material which bears a very close resemblance to the sillimanite of nature and, until quite recently, was regarded as identical with it. In the manufacture of various sorts of refractory articles, this material was a desirable constituent because of some of its very useful properties so that the conditions under which it could be formed and its general properties were of interest.

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[1] Research Associate, Dept. of Physics, Massachusetts Institute of Technology. Recd. May 20, 1925.

A short time ago, however, Bowen and Greig[1] published the results of some experiments indicating that the compound produced artificially was a material distinct from the natural sillimanite and they gave it the name "mullite." Mullite crystals were of the same orthorhombic form as sillimanite, but the indices of refraction were slightly different. A chemical analysis showed that its composition corresponded to a compound containing three molecules of alumina and two of silica. Table I shows the differences between sillimanite and mullite found by Bowen and Greig.

TABLE I

TABLE SHOWING PROPERTIES OF SILLIMANITE AND MULLITE

	Sillimanite	Mullite
Form	Orthorhombic	Orthorhombic
Prism angle 110 Λ $1\bar{1}0$	88°15′	89°13′
Per cent SiO_2	36.8*	27.5*
Per cent Al_2O_3	62.9*	73.0*
Index of Refraction γ	1.677	1.654
Index of Refraction α	1.657	1.642
Cleavage parallel to	010	010

* Average values.

Several other investigators have reported a chemical composition of the artificial compound which differed from the natural but the work of Bowen and Greig is unquestionably the most precise.

It was the purpose of the present investigation to compare the X-ray diffraction pattern of natural sillimanite with those obtained from the artificial compounds prepared in a number of different ways. The X-ray diffraction pattern produced by a crystalline material is characteristic of the arrangement of the atoms of the material and no two different materials have yet been found which give identical patterns.

Method

The method employed for the examination of the crystal structure of the alumina-silica compounds is that of Hull.[2] The atoms of a crystal are arranged in space according to a definite pattern and this pattern is repeated throughout each crystal grain. It has been found that X-rays are diffracted by the regularly arranged atoms in such a fashion that a measurement of the angles of the diffracted beams makes it possible to calculate the actual distance apart of the atoms, and the way in which they are arranged. It is necessary in order to obtain a diffracted beam from a crystal, that the axes of the crystal make certain definite angles with the X-ray beam, and to this end the method of Hull employs a sample composed of very fine crystal grains arranged in a perfectly random or chaotic fashion so that there are grains of every possible orientation with respect to the original beam. It is thus possible to record on a photographic film all the diffracted beams at one time and such a record is known as the diffraction pattern of the particular sample. A detailed account of this process has been ably set forth in the very excellent work of R. W. G. Wyckoff.[1]

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[1] Bowen and Greig, "The System Al_2O_3–SiO_2," *Jour. Amer. Ceram. Soc.*, **7** [4], 238 (1924).

[2] Hull, "A New Method of X-Ray Crystal Analysis," *Phys. Rev.*, **10**, 661 (1917).

The apparatus employed for obtaining the diffraction patterns was the General Electric Company's X-ray diffraction apparatus which has been described by W. P. Davey.[2] The characteristic radiation of molybdenum is used as the X-ray beam and a film holder 8 inches in radius gives a good separation between the diffraction lines on the film.

A number of different methods of mounting the sample of crystalline material have been employed. Because of the construction of the instrument, it is necessary to allow the size of the sample to determine the width of the diffraction lines on the film and the usual manner of mounting is to grind the sample very finely and place it in a small glass tube. Two other methods were employed in this investigation, one consisting of grinding a portion of the fused sample to a blunt chisel edge and mounting in the film holder in such a manner that this edge was in the center of the X-ray beam and also the center of the cylinder on which the film was wrapped. Under proper conditions of cooling, the fused sample contained fine crystal grains in random orientation. The other method consisted of grinding the sample to a very fine powder, mixing it with some non-crystalline binder, such as glue, and depositing it thickly on the edge of a card. This card was mounted in the film holder as before. The former method gave bright lines which extended nearly the whole length of the film, but they were rather broad. The latter method gave weaker lines but they were much more sharply defined, and could be measured with accuracy. An exposure of about 300–350 milli-ampere-hours was required for a good pattern.

Results

As a result of the examination of about 50 films, it has been found that the patterns given by mixtures of pure Al_2O_3 and SiO_2 in the molecular proportions of 3:2 and 1:1 heated to temperatures from 1500° to 1850°C as well as samples of fused kaolin and other pure clays are alike and are identical with the pattern obtained from a sample of natural sillimanite from Norwich, Conn.

The agreement was exact both in the position of the lines and in their relative intensities within the experimental error. The only exception was a sample of the 3:2 mixture which was heated to fusion in a carbon tube resistance furnace for a considerable time. It was thought that since silica is easily driven off under these conditions, the pattern would correspond to that of corundum. The pattern was found to check exactly with the pattern given by fused C.P. Al_2O_3 as well as fused bauxite and diaspore whose crystalline component is chiefly corundum. These results are best shown by the following table:

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[1] Wyckoff, "The Structure of Crystals," The Chemical Catalog Company, New York, 1924.

[2] Davey, "A New X-Ray Diffraction Apparatus," *Gen. Elec. Rev.*, 565, Sept. (1922).

TABLE II

Sillimanite		Artificial compound	
Spacing (A.U.)	Intensity	Spacing (A.U.)	Intensity)
3.45	Strong	3.44	Strong
2.91	Faint	2.91	Faint
2.69	Medium	2.72	Medium
2.55	Strong	2.55	Strong
2.43	Faint	2.38	Faint
2.30	Very faint	....	.....
2.21	Strong	2.22	Strong
2.12	Medium	2.10	Medium
1.70	Medium	1.72	Medium
1.60	Medium	1.61	Strong
1.57	Faint	....	.....
1.52	Strong	1.52	Strong
1.45	Medium	1.45	Medium
1.38	Faint	1.38	Faint
1.33	Strong	1.34	Medium
1.27	Medium	1.27	Medium
1.25	Faint	1.24	Faint
1.18	Faint	1.19	Faint
1.14	Very faint	1.14	Faint
1.12	Very faint	1.12	Very faint
1.10	Medium	1.10	Medium
1.05	Very faint	1.04	Faint
1.01	Medium	1.01	Medium

The spacings tabulated in the above table are the distances apart of the planes in the crystal which produce the diffraction lines. Each line on the film corresponds to a certain distance between atoms in the crystal. The figures in the table are averages of a number of different films, and were recorded by three different observers. The agreement of the two sets of data is as close as would be expected of two different observers measuring

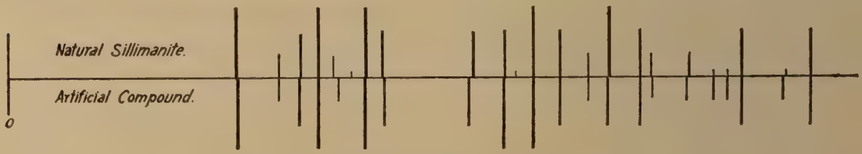

FIG. 1.—Plot of the spacings of Table II.

the same film. Figure 1 shows the diffraction lines of the two patterns plotted to scale. The height of each line is a measure of its intensity. Figure 2 shows a comparison of some of the films.

Conclusions

The conclusion is drawn that the only compound of alumina and silica which is formed under the conditions of these experiments gives an X-ray diffraction pattern which is identical with natural sillimanite. This has been previously observed by G. Shearer.[1] From this it follows that the regularly arranged atoms in these two compounds must have exactly the same positions in space. Unfortunately, because of the great complexity of the pattern, it has not yet been possible to work out this arrangement, but it is hoped that this may be accomplished in the future. Some large single crystals with faces about $^1/_2$ inch square would be very useful in this connection. If the regularly arranged part of the molecule of compound is the same in each case, the only way in which the difference in chemical analysis which has been observed may be accounted for is by assuming that in the open spaces of the molecule there are placed additional silica or alumina molecules. These must be arranged at random for they do not give a diffraction pattern and there must be substantially the same number in different molecules of compound to account for the quite exact ration of 3:2 or 1:1 which has been found. These two conditions are almost contradictory. If such groups of atoms were present and arranged in a random manner they would cause considerable general scattering of the X-ray beam. This would produce a blackening of the film at the lower end and no such effect has been observed. The only other conclusion is that the two compounds are identical and this is in direct contradiction of the accurate chemical analyses of Bowen

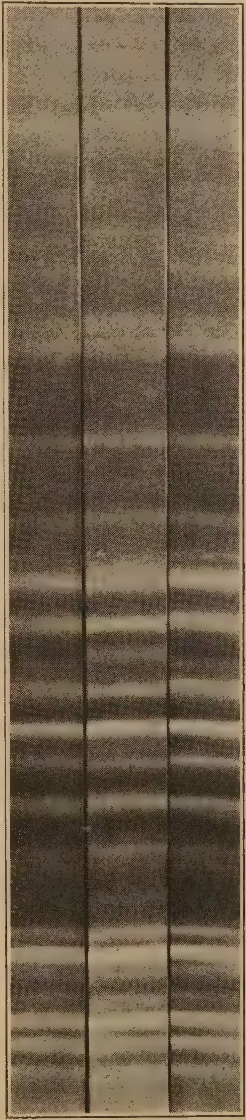

FIG. 2.—Comparison of diffraction films. Upper pattern is that of a 1:1 mixture, center is natural sillimanite, and the lower pattern is that of a 3:2 mixture.

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[1] G. Shearer, "X-Ray Investigation of China Clays," *Trans. Cer. Soc.* (Eng.), **23,** 314 (1923–24).

and Greig. . It seems as if the X-ray method of analysis was a more fundamental method of determining the nature of a substance than a chemical method in this particular case because the results are properties of the crystalline phase only, and are not upset in any way by the amorphous glass in which these crystals occur or which they may include.

It is not possible to tell from the results obtained so far, whether the fundamental lattice which gives the observed diffraction pattern corresponds to the 3:2 or the 1:1 ratio. It is a simple matter to calculate where the diffraction lines should be if the space lattice of the crystal is known, but to reverse the process is not at all simple. Some measurements on single crystals are necessary before this problem can be solved. However, if the lattice constants are completely determined, comparison of the size of the unit cell of the lattice with that calculated from density observations should completely answer this still rather perplexing question.

In closing, I wish to acknowledge the assistance rendered by C. L. Norton, Jr., and E. R. C. Ward, in the course of this investigation.

CHANGES IN THE CONSTITUTION AND MICROSTRUCTURE OF ANDALUSITE, CYANITE, AND SILLIMANITE AT HIGH TEMPERATURES AND THEIR SIGNIFICANCE IN INDUSTRIAL PRACTICE*

By Albert B. Peck

ABSTRACT

Owing to their growing commercial importance in the manufacture of refractories and porcelain, the minerals of the sillimanite group (andalusite, cyanite, and sillimanite) were investigated as to their decomposition products and volume changes between cones 10 and 15.

Petrographic-microscopic examinations showed that andalusite breaks down at cone 13 into mullite and glass, while cyanite also breaks down into the same components but at cone 12. Sillimanite is not decomposed up to cone 15. The composition of the mullite was checked by chemical analysis.

Andalusite shows almost no volume change at dissociation; sillimanite shows a slight expansion up to cone 15; cyanite shows a great expansion and disintegration at dissociation.

The practical significance of the behavior of the minerals is discussed as well as their possibilities of use in ceramic ware. Andalusite could be used in the raw state; cyanite would require calcination before use, so that andalusite appears to be best suited for most bodies.

Introduction

As a result of heating at high temperatures or of fusion at atmospheric pressure, many aluminium silicate minerals including andalusite, cyanite, topaz, dumortierite, kaolin and others invert or break down into other substances. One product of this change is a crystalline compound which until very recently has been interpreted as artificially produced sillimanite with the composition $Al_2O_3.SiO_2$. A knowledge of the conditions under which this alteration takes place is very important because of the use of some of these minerals in industrial processes. This is especially true of the trimorphous group of minerals, andalusite, cyanite and sillimanite, with which this paper is concerned.

The compound $Al_2O_3.SiO_2$ is trimorphous forming a group of three minerals, andalusite, cyanite and sillimanite, generally referred to in the literature as the sillimanite group. These minerals, while of the same empirical chemical formula, differ crystallographically. Two of them. andalusite and sillimanite, are orthorhombic in crystallization forming somewhat similar crystals which, however, can be differentiated by accurate measurement of their interfacial angles. The third mineral, cyanite, is triclinic, having a typical crystal form and certain very distinctive physical properties. The optical constants of these minerals, however, allow complete differentiation to be made.

From the geological standpoint, the type of rocks in which these minerals occur, leaves no doubt that they have been formed under different con-

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* Recd. May 29, 1925.

ditions and that they therefore might be expected to react differently when heated. In nature sillimanite is apparently more stable than cyanite and andalusite toward heat. This has also been observed to be the case under the artificial conditions of the laboratory.

Industrial Aspect of the Investigation

A crystalline constituent having optical properties very similar to sillimanite has been observed as one of the components of many ceramic wares for a long time. This constituent has usually been referred to as "artificial sillimanite." It was also a commonly known fact that the good qualities of many porcelains were due, at least in part, to the formation of this compound. Accordingly, the development of any method or the use of any material which increases the amount of this compound in the ware necessarily becomes of great value in industrial practice.

For some years, therefore, the manufacture of special types of porcelain has tended toward the formation, during firing, of an increasingly higher content of "artificial sillimanite." Bowen and Greig[1] have recently shown, however, that its composition is not the same as natural sillimanite ($Al_2O_3.SiO_2$) as previously supposed but rather is $3Al_2O_3.2SiO_2$. Their work showed that the two compounds are not only similar chemically but also strikingly similar optically.

"Artificial sillimanite" as produced in ceramic ware usually results from molecular changes taking place in clay under the influence of heat and various fluxes. The highest content of "sillimanite" has been developed by introducing into the unfired body artificially prepared "sillimanite" in the form of a calcine or the product of direct fusion. Although this method has been in use for several years in the manufacture of spark plug porcelains, it was of course an expensive way to obtain the desired end.

In order to eliminate the necessity of making an "artificial sillimanite" to be introduced into the body, the logical procedure was to attempt to employ one of the natural Al_2SiO_5 compounds, namely, andalusite, cyanite or sillimanite. However, the difficulty of obtaining any of these minerals in sufficiently large quantities and in a pure state was not overcome until recently when a large deposit of andalusite was located in California. It was then possible to substitute the natural material for the "artificial sillimanite." Undoubtedly andalusite will be used in the future for other purposes as well.

As a result of the discovery of this new deposit, a knowledge of the temperatures or points at which the different members of the sillimanite group break down is important from the industrial standpoint in three ways.

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[1] N. L. Bowen and J. W. Greig, "The System Al_2O_3–SiO_2," *Jour. Amer. Ceram. Soc.*, **7** [4], 238 (1924).

First, it is desirable to know in each instance what products are formed as a result of the breakdown of these minerals. This must be known in order to approach other problems more intelligently.

Second, it is also important to know (*a*) at what temperature decomposition is complete; (*b*) whether this point is reasonably stationary and the breakdown sharp; (*c*) whether the breakdown is slow and persists over a range of temperature.

Third, because of accompanying volume changes in the material at its decomposition point, these changes as well as the actual point of breakdown are important. In order that volume changes may be fully stabilized it is necessary to carry the firing of the ware well beyond the decomposition point, especially if the volume change is large and takes place slowly.

Review of Literature A review of the literature reveals the fact that the investigations of the effect of heat upon minerals of the sillimanite group range from simple descriptions of the loss of color of the minerals when heated in the blow-pipe flame, to various attempts to form the minerals synthetically. The most recent work of this kind is that of Bowen and Greig upon the revision of the system $Al_2O_3.SiO_2$ and the true nature of the compounds formed in the breakdown of sillimanite.

Apparently no attempt has been made to correlate the changes involved with practical ceramics except in the work of Bowen and Greig. This is no doubt due to the fact that only quite recently have any of the minerals of the sillimanite group been used in the manufacture of ceramic ware. To be sure, the presence in ceramic bodies of what has been called sillimanite has been known for a long time, but this substance has developed as a by-product of the molecular decomposition of clay and has recently been shown by Bowen to be not "sillimanite" but actually a compound of the composition $3Al_2O_3.2SiO_2$. For some years so-called "artificial sillimanite" has been manufactured from its oxides or from clay for subsequent use in ceramic ware.[2] This "sillimanite," however, is a synthetic product which should not be confused with the natural minerals.

Methods Used and the Changes Involved

In the study of the effect of heat upon minerals of the sillimanite group, three general methods of attack appear to have been used. These methods may be designated as physical, physical-optical, and physical-chemical-optical. A fourth method (chemical-optical) does not appear to have been used in investigations of changes in the natural minerals although it has been used extensively in the study of artificially formed "sillimanite."

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[2] A. V. Bleininger and F. H. Riddle, "Special Spark Plug Porcelains," *Jour. Amer. Ceram. Soc.*, **2**, 564 (1919).

Vernadsky[3] summarizes excellently the various attempts of investigators up to 1889.

Physical This represents the earliest type of study and consists largely in simply recording observations of the loss of color and of the whitening effect of minerals when subjected to the blow-pipe flame. This of course represents a very crude method of determining what changes had taken place; in fact, there seems to be no evidence that there was any serious effort among the earliest observers to follow the matter further.

According to Vernadsky, Saussure,[4] who first found and described cyanite, observed that needles of cyanite, "losing to fire their color, whatever it may be, change to a dull white. They show a granular texture which renders them somewhat fragile." Many others make practically the same statement. Some ascribed the change to the decomposition of pigments and minerals included in the cyanite. Laugier[5] and Erdmann[6] reported losses in weight, sometimes as high as 0.61%. Vernadsky confirmed this and interpreted the loss in weight as possibly indicating that the change may in part be due to the loss of some volatile constituent.

Many mineralogists record that andalusite does not lose its original compactness but simply whitens. The same is true of sillimanite.

Physical-Optical This method makes use of alterations taking place, under the influence of heat, in the physical properties such as hardness and specific gravity. These alterations are further supplemented by changes in optical properties.

Vernadsky used a method of this character in his work on cyanite. He found that first, the average hardness of the mineral increased slightly; second, the specific gravity diminished markedly; and third, the fragments showed distinct changes in optical properties. Curiously enough he does not appear to have observed the optical property which is generally considered most important of all, namely, the index of refraction. As a result of this work Vernadsky was able to make the statement that "heated to a determined temperature (about 1200–1330°C), cyanite changes to another mineral which is probably sillimanite." Apparently he had no way of accurately controlling the temperature in these experiments, hence the wide range of temperature mentioned. He also states that sillimanite, and probably also andalusite, is stable at this temperature.

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[3] W. Vernadsky, "Note sur l'influence de la haute temperature sur le disthene," *Bull. Soc. Fr. Miner.*, **12,** 447–56(1889).

[4] Saussure, "Voyage dans les Alpes," **4,** 84–5, Neuch. (1796).

[5] Laugier, "Analyse de disthene du St. Gothard," *Ann. du Mus.*, **5,** 13 (1804).

[6] Erdmann, "Undersokning af några Lerjordssilikater," *Sv. Akad. Vet. Handl.*, **24** (1843).

Physical-Chemical-Optical

Much credit for the development of this method as a means of investigation belongs to the staff of the Geophysical Laboratory of the Carnegie Institution. The method is essentially synthetic. It involves building up the various binary and ternary compounds from their oxides, and determining all important optical and physical properties, such as melting points of compounds and eutectics, dissociation points, inversion points, and so forth. Thus, the effects of variation in temperature and chemical composition are not only very accurately controlled but they are also supplemented by petrographic-microscopic examination.

Although this method was originally designed as a basis for further detailed study of petrologic problems from the standpoint of pure science, experience has shown that many of the methods developed and the results obtained by the above investigators can be applied to industrial, especially ceramic, problems either in explanation of existing conditions or as aids in research. Their work on the system Al_2O_3–SiO_2 has an important bearing in this connection.

One of the earliest investigations using the physical-chemical-optical method was conducted on the system Al_2O_3–SiO_2.[7] The results of this work seemed to indicate that there was only one compound of Al_2O_3 and SiO_2, namely, $Al_2O_3.SiO_2$, corresponding in most of its optical properties to the natural mineral sillimanite. Certain minor discrepancies somewhat difficult of explanation were observed. Thus, it was never possible to obtain the compound in a perfectly pure state, small amounts of glass always being present. Also the refractive indices of the artificial crystals were distinctly lower than those of the natural mineral. Owing to the fact that chemically pure oxides were used, the observed optical properties were probably assumed to represent the true constants of the synthetic compound $Al_2O_3.SiO_2$, although they were quite different in some respects from those of natural sillimanite. Variations in the natural mineral were thought to be due to impurities. The presence of glass was explained by the high melting point of the compound, since, because of the high temperature at which it began to crystallize and on account of the apparently rapid rate of crystallization, some glass might easily be included between the fibrous crystals.

At the same time these investigators verified Vernadsky's statement that at high temperatures both andalusite and cyanite undergo changes to another form, probably to sillimanite. The exact temperatures of the changes were not definitely determined, except that they are somewhere between 1150° and 1500°C. Various fluxes apparently decomposed the minerals before the change took place. They were not, however, able to verify the statement that when andalusite undergoes this change an evolution of heat occurs.

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[7] Shepherd, Rankin and Wright, "The Binary Systems of Alumina with Silica, Lime and Magnesia," *Am. J. Sci.*, **28**, 302 (1909).

The work on the system Al_2O_3–SiO_2 was quite generally accepted until recently when Bowen and Greig in a revision of this system showed that the former conception was inaccurate, and that although there was but one compound formed between Al_2O_3 and SiO_2, it is not $Al_2O_3.SiO_2$, but rather $3Al_2O_3.2SiO_2$. From the melt of mixtures of the two oxides in these proportions only one component results, which is entirely crystalline and possesses the optical constants previously assigned to the "sillimanite" of the earlier work on the same system. The establishment of this fact immediately explained the discrepancies in the earlier study, such as the lower refractive indices of the so-called artificial sillimanite and the presence of excess glass in the melt of the 1:1 mixture.

Furthermore, Bowen and Greig showed that at 1545°C natural sillimanite melts incongruently and breaks down into $3Al_2O_3.2SiO_2$ and excess siliceous glass. At the same time they examined the "sillimanite" which had been produced in ceramic ware of various kinds and found that in each case it was not $Al_2O_3.SiO_2$ but the new compound $3Al_2O_3.2SiO_2$. Subsequently this new compound was also found to exist in certain fused argillaceous rocks and was given the name mullite.[8] Thus, although the compound $Al_2O_3.SiO_2$ exists in nature in three different crystalline forms, none of them have yet been produced in the laboratory.

Sillimanite and Mullite in Ceramic Ware

As already pointed out, the presence of a crystalline compound, having properties very similar to those of sillimanite, has been recorded in ceramic literature for about fifty years. Since its presence was first noted, the occurrence of this compound in ceramic bodies has been studied from many angles. Its importance in lending valuable properties to the ware has become recognized more and more until recently a microscopic description of a ceramic body was not considered complete without some reference to the so-called sillimanite.

Behrens[9] was apparently the first to make a microscopic study of porcelain, the results of which were published in 1873. He stated that the groundmass of molten feldspar undergoes devitrification, and that the material which separated from the groundmass dissolved in hydrofluoric acid less readily than the quartz and glass present. He did not identify the crystals, but his description of their insolubility suggests crystals of "sillimanite."

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[8] Bowen, Greig and Zies, "Mullite, A Silicate of Alumina," *J. Wash. Acad. Sci.*, **14,** 183 (1924).

[9] H. Behrens, "Ueber das porcellan und einige verwandte entglasserungsproduckte," *Pogg. Ann.*, **150,** 386 (1873).

In a microscopic study of porcelain, Hussak in 1889[10] described the presence of needle-like crystals, very minute and weakly doubly refracting, resembling sillimanite. Mellor[11] in 1907 reported "sillimanite" in Chinese and Berlin porcelains.

Plenske[12] in an elaborate study of porcelains, published in 1908, noted that porcelains could be divided into groups according to the presence or absence of crystalline products in the groundmass. Furthermore, he observed that "sillimanite" might also be present in masses of exceedingly minute grains which were apparently amorphous. Plenske also believed that the crystalline "sillimanite" was formed by devitrification of the glassy groundmass.

Zoellner,[13] also in 1908, identified optically the occurrence of "sillimanite" in porcelain, and also separated the crystals by hydrofluoric acid. He found that the ratio of Al_2O_3:SiO_2 was 1:1. He believed that the "sillimanite" was formed by a molecular change in the clay in the body and not through devitrification.

More recently in 1916, Klein[14] made a detailed study of various types of porcelain and the relation of the development of "sillimanite" in them to the temperature of firing. Riddle[15] in 1919 also described the presence of "sillimanite" and its relation to various fluxes and fine grinding. Of recent years reports of the development of "sillimanite" in porcelains have become very numerous.

"Sillimanite" has also been reported in other ceramic bodies besides porcelain. In 1890 Vernadsky[16] called attention to its formation from the heating of clay. In 1919 Cox[17] claimed to have found it in fire clay exposed to a high temperature for a long period, although the chemical analysis which he gave did not indicate a ratio of 1:1 for the constituent oxides but was more nearly 3:2, namely, that of mullite. Mellor[18] at various times has reported its formation in fire brick. Many references might also be given in which its presence in glass is reported. In these cases its formation is believed to be due to the decomposition of clay from the tank or pot walls by the glass.

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[10] E. Hussak, *Sprechsaal,* 153 (1889).

[11] J. W. Mellor, "Some Chemical and Physical Changes in Firing Pottery," *J. Soc. Chem. Ind.,* **26,** 375 (1907).

[12] E. Plenske, "Ueber mikrostruktur und bildung des porzellans," *Tonind. Ztg.,* 1343 (1908); *Sprechsaal,* **41** [Nos. 20, 21, 22] (1908).

[13] A. Zoellner, "Zur frage nach der chemische-physikalischen natur des porzellans," *Chemische Industrie,* 212 (1908).

[14] A. A. Klein, "Constitution and Microstructure of Porcelain," U. S. Bur. Stand., *Tech. Paper* **80** (1916).

[15] F. H. Riddle, "Further Studies of Porcelain," *Jour. Amer. Ceram. Soc.,* **2,** 812 (1919).

[16] W. Vernadsky, "Sur la reproduction de la sillimanite," *Bull. Soc. Fr. Miner.,* **13,** 256–71 (1890).

[17] A. H. Cox, "Note on Some South Staffordshire Fire Clays and Their Behavior on Ignition," *Geol. Mag.,* **5,** 61 (1918).

However, as already mentioned, it remained for Bowen and Greig to point out that the "sillimanite" in all the bodies examined by them was not of the composition $Al_2O_3.SiO_2$, but $3Al_2O_3.2SiO_2$, now called artificial mullite. They were also fortunate in obtaining from an outside source some well crystallized $3Al_2O_3.2SiO_2$, which was used to measure accurately both the crystallographic and optical constants and to show its very close similarity to natural sillimanite.

Present Investigation

Purpose The purpose of the present investigation is not to establish the exact temperatures at which andalusite, cyanite, and sillimanite undergo change but rather to establish, first, the nature of the resulting product; second, the points at which decomposition takes place, and whether this decomposition is a sharp change or covers a range of temperature; third, the character of the accompanying volume changes. Any of these changes, when produced under industrial conditions, may take place at quite different temperatures than under the more exactly controlled conditions of the laboratory devoted to pure science.

Method Used Owing to the accurate and detailed information available on the compounds developed in the system Al_2O_3–SiO_2 as worked out at the Geophysical Laboratory, the method used for the preparation of the samples and later identification of the resulting products was comparatively simple, involving four steps as follows:

1. Powdered samples of the raw materials were first fired to predetermined temperatures in open crucibles.
2. A careful petrographic-microscopic examination of each of these firings was made, using the method of immersed grains.
3. The crystalline products formed from andalusite and cyanite were analyzed chemically, affording evidence in addition to the work of Bowen and Greig on sillimanite.
4. Determinations were made of the changes in specific gravity between the unfired and fired minerals.

Firing The kiln in which the minerals were fired is a large laboratory kiln designed by the Champion Porcelain Company, for research work and for the accurate reproduction of conditions in full sized kilns. It is of the down-draft type.

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[18] J. W. Mellor, *loc. cit.* (11); "Some Notes on the Action of Heat on Fire Clays," *Clay and Pottery Industry*, 909–15.

In overall size it is 8 feet high, 6 feet wide, and 4 feet 6 inches deep. The chamber is 3 feet 6 inches high, 3 feet 6 inches wide, and 1 foot $6^1/_2$ inches deep, and has a capacity of seven 15-inch by 5-inch saggers.

Thermoelement pyrometer contról is provided through several openings. Cone 32 may be fused in this kiln.

The minerals were fired in small open crucibles each containing about five grams of material. Two series of firings were made, after the manner of draw trials. The first series of drawings was started at cone 8 and continued every two cones thereafter inclusive of cone 16. Orton cones were used.

The microscopic examination of these firings showed that no changes were to be observed in the minerals below cone 11, and further that in andalusite and cyanite the changes were completed between cones 12 and 14. Sillimanite, however, showed no decomposition even at the highest temperature.

Having thus established the upper and lower limits of the changes in andalusite and cyanite, a second series of draw-trials was made from cones 10 to 15 inclusive, with samples taken at every cone. It was on these samples that the petrographic-microscopic examinations described later were carried out.

Observations on the Material Used

A. Andalusite

The andalusite which was used in these firings came from the mine owned by the Champion Porcelain Company and located on White Mountain of the Inyo Range, Mono County, California. A complete description of the crystallography and mineralogy of this andalusite has been given elsewhere.[19]

Since the andalusite, as received from the mine, is in the form of large fragments, it was necessary to crush it and then to grind the coarse granules without water to a fine powder in a pebble mill. As it was not desired to use the material in a body, and as grains of any size could be studied on the microscope slide, no attempt was made to screen and size it. The powder consisted of about 80% andalusite with minor amounts of pyrophyllite, mica, corundum, and rutile.

Effect of Firing The above powder, after being fired as previously indicated, was subjected to a careful petrographic-microscopic examination with results which follow.

At cone 10 the only apparent outward change is a slight consolidation of the powder into a firm but quite brittle mass. The microscopical examination shows no change in the andalusite grains. They still remain clear and retain all their original optical properties.

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[19] A. B. Peck, "Note on Andalusite from California; a New Use and Some Thermal Properties," *Am. Mineral.*, 9 123–9 (1924).

The plates of mica have decomposed into masses of exceedingly minute rounded grains embedded in a glassy matrix, and are quite similar in appearance to the products of the breakdown as it first occurs in kaolin upon hard firing. These granular masses show no double refraction and both constituents are too fine-grained to identify.

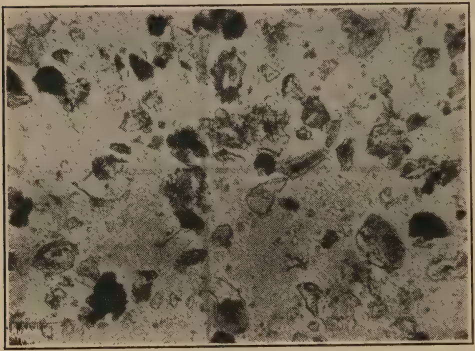

FIG. 1.—Andalusite, cone 12. Note the clear unaltered grains. The black grains are mica which has decomposed. Magnification 90.

At cones 11 and 12 there still is no outward change in appearance, nor is there any change in the optical properties of the andalusite grains. Due to the higher temperature of firing, the plates of mica show the grains resulting from the breakdown to be somewhat enlarged. Some of these grains are slightly elongated, the long direction being perpendicular to the original cleavage of the mica. Although they are still too minute for complete identification, their optical elongation can be determined as negative. (Figs. 1 and 2.)

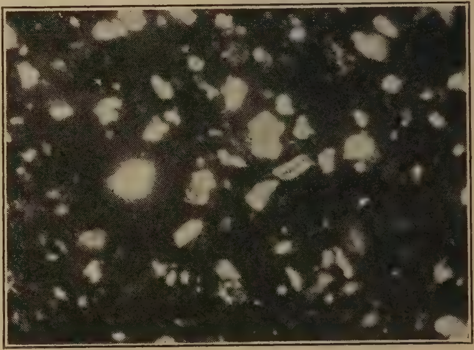

FIG. 2.—Same field as Fig. 1 taken with crossed nicols. Note the strong double refraction of the andalusite.

With an increase to cone 13, the mass in the crucible is a distinctly firmer body than in previous firings, a slight amount of sintering having taken place.

Microscopically, the andalusite also is noticeably altered, about half the grains showing the changed character. As is to be expected, most of the smaller grains are decidedly altered while the larger ones may be only partially affected and even in some cases entirely unaffected. The change in the andalusite fragments is apparently due to a breakdown into two components. One of these is crystalline and more abundant, while the other is a glass and minor in amount.

The crystalline component occurs as elongated crystals parallel to each other throughout the whole grain where it is completely decomposed, so that extinction between crossed nicols is complete over the whole grain at the same time. Optically the indices of refraction are $\gamma = 1.657$ and $\alpha = 1.643$. The elongation is positive. On account of the small size of the crystals, other optical properties could not be determined. These facts indicate that the crystalline compound formed is artificial mullite, $3Al_2O_3.2SiO_2$, described by Bowen and Greig, and which they determined to be the decomposition product resulting from the heating of natural sillimanite above 1545°C. As already indicated, this compound heretofore supposed to be artificial sillimanite was also found by them in ceramic ware. (Figs. 3 and 4.)

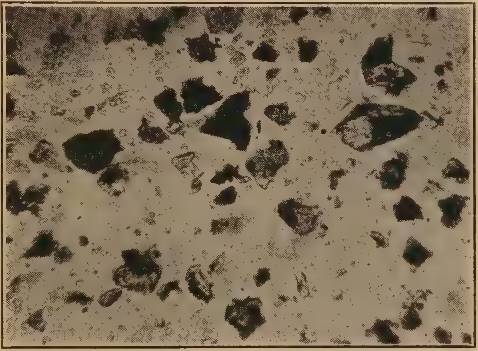

FIG. 3.—Andalusite, cone 13. Note that many of the grains are clouded and have a somewhat fibrous appearance due to decomposition with the formation of fibrous crystals of mullite with interstitial glass. Magnification 90.

The second component is isotropic in character and noncrystalline as far as can be determined. It is apparently a glass. Its refractive index is slightly variable, depending probably upon the character of the impurities present, and which have been taken into solution. In general the index is near 1.54. As pointed out by Bowen and Greig, this glass is probably very siliceous in composition.

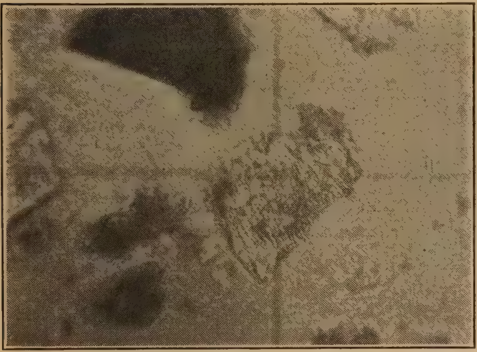

FIG. 4.—Andalusite, cone 13. The grain in the center of the preceding photograph magnified to 315 times, showing the detail of the parallel fibers of mullite extending across the grain.

As previously mentioned, not all the grains are decomposed to this mixture of crystals and glass. The change can sometimes be observed at an intermediate stage where grains show a fringe of parallel crystals around the outer edges with an unchanged center. The crystals in the fragment are not formed as radiating crystals but they are parallel throughout, without regard to the part of the grain in which they occur. The border consisting of crystals and glass does not have a definite boundary but passes irregularly and imperceptibly into unaltered andalusite at the center. Of interest also is the fact that the crystals which have formed in the andalusite grain, are of opposite optical orientation from the original grain. (Figs. 5 and 6.)

Heated to cone 14 the powdered mass shows an increased firmness but is still not solid. The microscopic examination indicates that the decomposition is complete in all of the smaller grains of andalusite and in most of the larger ones. The smaller grains show crystals of mullite which are slightly larger than those formed at cone 13. A few of the largest grains still possess unchanged centers with crystal borders, but these are uncommon. (Fig. 7.)

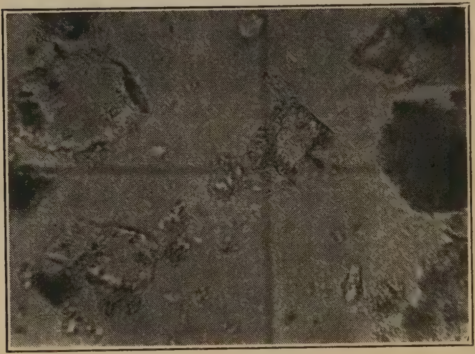

FIG. 5.—Andalusite, cone 13. Showing a grain having a decomposed border of fibrous crystals and glass, with a clear unaltered center. Magnification 315.

At cone 15 it is apparent that every grain is decomposed, even the largest and coarsest.

B. Cyanite

The cyanite used in these burns was obtained from Charlotte Court House, Virginia. Although the material is composed largely of cyanite, considerable amounts of quartz and a little muscovite mica are present as admixtures. Before being used commercially the crude material would probably require treatment to eliminate most of the quartz and mica, but for the purposes of the present work this was unnecessary.

Before firing, the material was ground to a powder but was not screened to any definite size, following the same procedure as with andalusite. This, however, did not affect the results as grains of the same size were considered in each case.

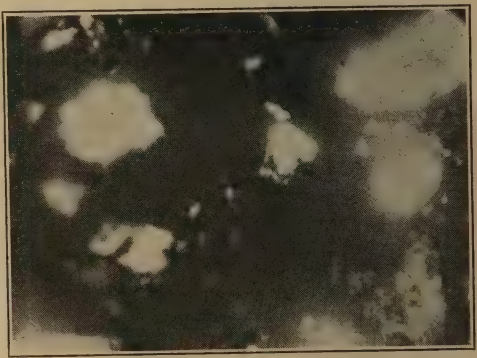

FIG. 6.—Same field as Fig. 5 taken with crossed nicols. Note the strong double refraction of the unchanged center and weaker double refraction of the fibrous border.

Effect of Firing Since all three members of the group were fired together the conditions were the same for cyanite as those described for andalusite.

At cone 10 the powder retains its slightly bluish green color. The cleavage surfaces of the larger grains can still be seen to be smooth and bright. The mass shows a very slight cohesion such as was noted in the corresponding burn of andalusite.

When examined microscopically no change in the optical properties of the fragments can be detected. They are still the same flat, straight-edged fragments, sometimes showing step-like terminations and cleavage cracks as in the unfired material. (Figs. 8 and 9.) The small amounts of mica present appear the same as in the andalusite fired at cone 10.

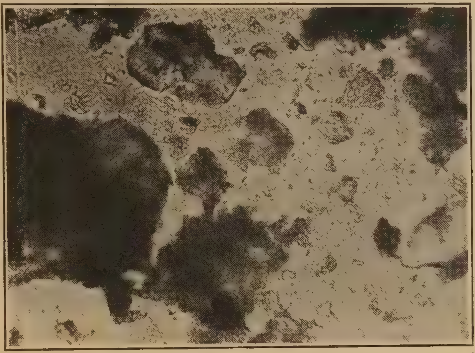

FIG. 7.—Andalusite, cone 14. Showing all grains to be decomposed to aggregates of parallel fibers as contrasted to the partial decomposition of some of the grains in the cone 13 burn, Fig. 3. Magnification 165.

At cone 11 there is still no outward change in the powder. Cleavage surfaces are bright and smooth for the most part, and the faint bluish color is present. Slight changes in microstructure appear to have commenced. Some fragments show the development of a few scattered fibrous crystals. These are similar in appearance to those formed in andalusite but are too far underdeveloped to make identification certain. Cleavage cracks in the fragments are somewhat more numerous, especially those perpendicular to the length of the grain. These are no doubt due to the expansion of the fragments under the influence of increasing temperature. The above evidence, though slight, suggests that a point is being approached where marked changes will take place.

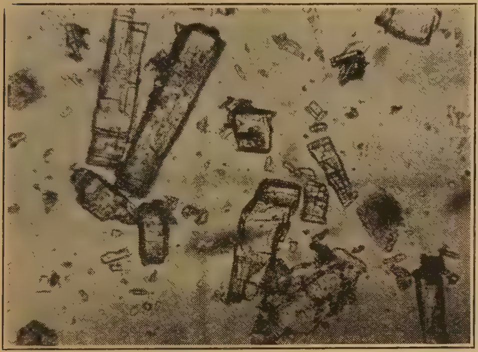

FIG. 8.—Cyanite, cone 10. Note the clear undecomposed grains and cleavage cracks. The black grains are mica as in Fig. 1. Magnification 90.

When fired to cone 12, the powder loses some of its color and assumes an external appearance slightly different from that of the preceding burn. Smooth, glistening cleavage surfaces are also less common. The microscopic decomposition is far more pronounced than would be suspected from the appearance of the powder alone. The fragments have broken up into irregular areas of crystals showing double refraction but these areas do not extinguish together. Only the largest grains show unchanged centers with altered borders. The small fragments show fibrous areas of elongated crystals, these areas being oriented in all directions and forming interlocking aggregates of needles. Hence, the fragments have a peculiar mottled appearance between crossed nicols. This is in distinct contrast to the marked parallelism of the crystals developed from andalusite. The crystals formed from cyanite have between them, as in andalusite, an amorphous, glass-like substance. The refractive indices of the crystals are $\gamma = 1.655$ and $\alpha = 1.642$. The glass has an index of 1.54. The elongation of the crystals is positive. As in the case of andalusite, other optical properties are not obtainable because of the small size of the crystals. Thus, from all indications optically both the crystals and the glass are the same components as are formed during the breakdown of andalusite. (Figs. 10 and 11.)

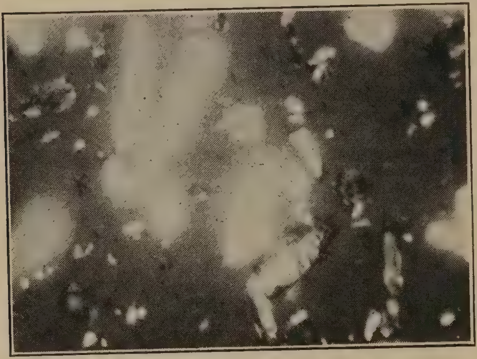

Fig. 9.—Same field as Fig. 8, showing the strong double refraction of cyanite.

At cone 13 there is a very pronounced external change in the powder. It becomes dull white in color and loses much of the slight cohesion it previously had. A large fragment fired along with the powder became dull white in color and very brittle, breaking down into many fragments during firing. These fragments when touched lightly, in turn crumble to a fine powder. This is due as pointed out by Vernadsky* to a pronounced expansion in volume and a decrease in specific gravity accompanying the change in constitution.

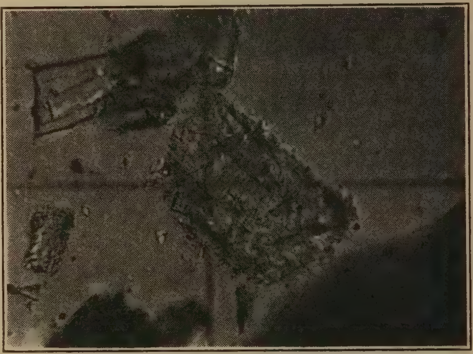

Fig. 10.—Cyanite, cone 12. Showing at high magnification the intimate detail of a grain of decomposed cyanite. Note that the fibrous crystals are not parallel as compared to those in decomposed andalusite (Figs. 3 and 4), but are intricately interlocking. The clear grain is quartz. Magnification 315.

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* W. Vernadsky, "Note sur l' influence de la haute temperature sur le disthene," *loc. cit.*

The microscopic examination reveals that the breakdown, which was well started at cone 12, has been entirely completed on the largest fragments. It shows, however, a more complete and definite development of variously oriented areas of mullite crystals and glass, and also that in many instances firing to the higher temperature has served to increase the size of the crystals.

No further marked change from cone 13 is apparent either externally or microscopically, at cones 14 or 15. In each case there is a tendency toward further growth in the size of the mullite crystals formed.

C. Sillimanite

The sillimanite used in firings covering the same range as those of andalusite and cyanite, was obtained from a recently reported Indian deposit, presumably from the Khasia Hills of Assam.[20]

It was used in the form of a fairly coarse powder with a grain size somewhat greater than the cyanite. The material was rather pure, consisting of irregular grains with an internal fibrous structure. Only a small amount of muscovite mica, quartz and iron oxides were present as impurities.

Effect of Firing

The firing was carried out in the same manner as for the other two members of the group.

As Bowen and Greig have pointed out, sillimanite does not decompose until a temperature of 1545°C has been reached, and since the maximum cone of the present series was only cone 15, no changes in structure were anticipated but the mineral was included mainly for the purpose of completeness.

At all cones including cone 15 the material remained a loose, incoherent sand, no hint of sintering being observed. There was no external change in the grains.

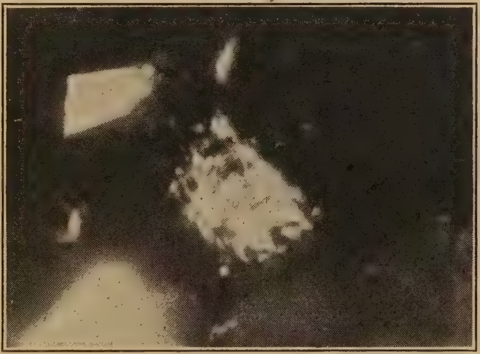

FIG. 11.—Same field as Fig. 10 taken with crossed nicols. Note the mottled appearance of the large grain in the center, due to variously oriented groups of fibers. Some are in extinction while others are light.

Under microscopic examination no decomposition could be detected even at cone 15, the grains at all times retaining the optical properties of sillimanite, losing none of their original structure, and showing no signs of a breakdown similar to the other two members of the group.

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[20] Anon., "Sillimanite: A High Grade Refractory," *Bull. Imperial Inst.*, **21**, 383 (1923); through *Ceram. Abs.*, **3** [1], 15 (1924).

Chemical Composition of Artificial Mullite

Although Bowen and Greig did not analyze the artificial mullite crystals which were developed by heating natural sillimanite, they did show that these crystals had the same optical properties as pure artificial mullite. They also separated and analyzed crystals produced in the firing of various types of ceramic ware, and showed that these too were the same as mullite except that small amounts of Fe_2O_3 and TiO_2 which had been taken into solid solution increased the indices of refraction of the crystals noticeably and also produced a violet or pink pleochroism.

Since the optical properties of the crystals formed by the dissociation of andalusite and cyanite are very similar to those of mullite, chemical analyses of them were made. The chief obstacle encountered in determining the composition of these crystals was due to their very minute size. This not only renders it difficult to free them from the admixed silica glass but appears to make the crystals themselves very susceptible to decomposition in cold hydrofluoric acid.

In the preliminary examination the crystals were exposed to cold hydrofluoric acid for one week, the fired material having been previously ground to a very fine powder. This treatment resulted in the complete decomposition of the crystals as well as the silica glass. Finally the method used by Vernadsky and adapted by Bowen[8] was followed, allowing the powder to stand in 25% hydrofluoric acid overnight at room temperature. After the crystals were freed from excess acid by repeated decantations, they were finally filtered off. Treated in this manner both the andalusite and cyanite firings gave fairly pure residues of mullite crystals. The former contained appreciable amounts of corundum, some undissociated andalusite, rutile and a little glass, while the latter showed a little decomposition of the crystals and a very little corundum.

The results of the chemical analyses given in the table below confirm the optical evidence.

	Composition of mullite crystals formed from		
	Andalusite	Cyanite	Theoretical for $3Al_2O_3.2SiO_2$
SiO_2 (corrected)	31.98	27.37	28.2
Al_2O_3 (corrected)	68.02	72.63	71.8
Corundum	1.50	1.39	
Rutile	1.77		

Thus, it is quite apparent that the agreement between the analyses and the theoretical composition is sufficiently close to warrant the composition of the crystals being placed at $3Al_2O_3.2SiO_2$. The more siliceous character of those obtained from the andalusite firing is mainly due to the presence of some andalusite which was not entirely decomposed during firing.

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[8] Bowen, Greig and Zeis, *loc. cit.*

There does not appear to be any method at present to determine andalusite separately, as can be done for corundum and rutile. The low SiO_2 in those from the cyanite is probably due to slight decomposition previous to analysis.

Attention is called particularly to the fact that TiO_2 is present as rutile and is not in solid solution in the mullite. This accounts for the fact that the indices of refraction of the mullite crystals do not vary appreciably from those of pure synthetic mullite, nor do these crystals exhibit the characteristic pleochroism of mullite containing TiO_2.

Changes in Specific Gravity as a Result of Firing

While very little change in volume was observed in the andalusite powder at its dissociation point, that which accompanied the dissociation of cyanite was very pronounced. This was more apparent when a comparison of the unfired and fired powders was made, as shown in the following table. The standard pycnometer method was used.

	Specific gravity	
	Unfired	Fired to cone 15
Andalusite	3.29	3.20
Cyanite	3.59	3.09
Sillimanite	3.15	2.92

It is quite apparent that cyanite is most affected as a result of heating, while sillimanite is affected much less and andalusite least of all.

The decrease in specific gravity in andalusite and cyanite is attributable directly to the dissociation. In sillimanite, however, no dissociation is apparent microscopically. The change, therefore, would seem to be due to the production of fine microscopic or submicroscopic cracks caused by the natural thermal expansion with increasing temperature or perhaps more likely still to volume changes in the associated minerals which were present in small amounts.

Summary of Changes during Firing

The results of the changes in constitution, microstructure, and volume of the members of the sillimanite group when fired up to cone 15 may be briefly summarized as follows.

Andalusite From the evidence furnished by the petrographic-microscopic examination of the various firings, it is certain that under the conditions detailed, andalusite breaks down rather abruptly at cone 13, yielding a mixture of mullite and a siliceous glass. The resulting structure is one of parallel crystals extending throughout the whole area of a grain of the mineral, with interstitial glass. If the grain be rather large, the center may be unchanged with a fringe of crystals and glass around the outer edges.

The optical orientation of the crystals thus formed is opposite to that of the original grain.

Firing to higher cones serves to enlarge the size of the crystals somewhat and to complete the breakdown of the larger grains.

The volume changes are small, only a slight expansion taking place.

Cyanite The change in cyanite does not appear to be as abrupt as in andalusite. The increase in the cleavage cracks crossing the length of the fragments and the incipient formation of fibrous crystals seem to indicate that at cone 11 a point is being approached where marked changes will occur. These changes actually occur at cone 12 but the microscopic changes are more pronounced than the megascopic appearance would indicate.

The same components are formed as in andalusite, namely, mullite and interstitial glass, but these constituents have developed an entirely different structure and relationship to the original grain from that observed in the andalusite. They occur in irregular areas, each grain frequently containing several crystal areas. In any one of these areas the crystals may be parallel to each other but of decidedly different orientation from that of the other areas in the same grain. Adjacent areas interlock more or less with each other.

There is a very marked increase in volume at the dissociation point, much greater than that which takes place in andalusite.

Sillimanite Sillimanite shows no change megascopically or microscopically, inclusive of cone 15. This is in complete accord with the observations of Bowen and Greig.

The volume change is not as great as in cyanite, but is greater than that of andalusite. Because no dissociation is observable microscopically, it seems probable that it is due in part to the formation of cracks produced by thermal expansion or to the associated minerals.

The Significance of the Changes

Monotropism and Ceramic Ware It has been shown that the minerals of the sillimanite group break down at certain points with accompanying mineralogical and volume changes. This brings up a factor which is of extreme importance from the practical standpoint, that of monotropism and its relation to ceramic ware.

If minerals undergo change or inversion to a different crystalline substance of identical chemical composition when heated below their melting or disintegration points, the change may be of two kinds; that is, it may be a temporary or a permanent change. In the case of a temporary change, where the original crystalline condition returns when the mineral is cooled, it is referred to as enantiotropic. If the change is permanent, the mineral is said to be monotropic in its reaction toward heat. In either case the change may be rapid or slow, a quality inherent in the substance itself.

The Silica Minerals

A classic example of enantiotropism and one which has a distinct bearing on the ceramic industry is that of the mineral quartz.[21] When quartz is heated or cooled a number of crystalline forms (seven in all) may be produced, depending upon the temperature and time factors. The more important of these inversions may be conveniently expressed in the following table. The inversion from the α- to the β-form of the same mineral is usually rapid while the change from one mineral to another is much slower.

α-quartz $\rightleftarrows$ β-quartz	570–575°C	rapid
β-quartz $\rightleftarrows$ β_2-tridymite	870	slow
β_2-tridymite $\rightleftarrows$ β-cristobalite	1470	slow
β-cristobalite $\rightleftarrows$ glass	1710	

In the absence of a flux the change from β_2-tridymite to β-cristobalite is easier than that from β-quartz to β_2-tridymite, hence we frequently find that β-quartz may invert to β-cristobalite without passing through the β_2-tridymite stage. This is what happens ordinarily in the original firing of silica brick. The tridymite develops in them in large measure subsequent to rather than before the formation of cristobalite, under conditions of long continued heating at some temperature above 870°C and below 1470°C.[22] Moreover, the greatest expansion in silica brick takes place when quartz inverts to one of the tridymite or cristobalite forms. Thus, although the silica minerals are enantiotropic, the reversion is so slow that once inversion has been accomplished to tridymite or cristobalite, the ware takes on practically a monotropic character.

Sillimanite Group Is Essentially Monotropic

As has been previously shown, when any of the members of the sillimanite group are subjected to heating to certain temperatures which vary with the different minerals, each one breaks up into two substances. One is artificial mullite of the composition $3Al_2O_3.2SiO_2$. The other is a glass of a highly siliceous nature occurring as interstitial matter between the crystals. The crystalline substance formed in each case apparently has the same composition. This is also true of the glass. Strictly speaking, therefore, we cannot say that the members of the sillimanite group are monotropic in character because they break down and yield two substances differing in chemical composition from that of the original mineral. However, neither under conditions of slow or rapid cooling do these two compounds unite to form one compound having the properties of any member of the sillimanite group but they remain unchanged. Therefore, for all practical purposes, from the ceramic standpoint, the members of the sillimanite group may be considered as monotropic toward heat. Although consisting of two compounds, the end product is the same in all cases.

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[21] C. N. Fenner, "The Stability Relations of the Silica Minerals," *Am. J. Sci.*, **36,** 331 (1913).

[22] H. Insley and A. A. Klein, "Constitution and Microstructure of Silica Brick and Changes Involved through Repeated Burnings at High Temperatures," U. S. Bur. Stand., *Tech. Paper* **124** (1919).

Practical Significance of the Changes

Importance of Monotropism in Ceramic Ware

One of the chief requirements of ceramic ware is that it must be monotropic or practically so toward heat. This is especially true in the case of refractories. If a ceramic body is not monotropic, the oscillation or alternation of conditions would cause variations in the physical properties of some or all of the constituents of the refractory or other body to meet those conditions. Thus, undue expansion or contraction may be produced by a change in mineralogical composition. Hence the special monotropic character of the sillimanite group after firings to the cones indicated, is particularly valuable to the ceramist.

Importance of Volume Changes

In this connection also, the volume changes occurring in andalusite, cyanite, and sillimanite may be of as great significance as the actual mineralogical changes in the practical use of these minerals. Thus, if cyanite were used in a body, it would show a large and sudden expansion at cone 12 and great strains would be set up, accompanied by the production of cracks. The result of this would be a weak, porous, and "punky" body, as is the case of many silica bricks which have been fired too rapidly. In order to correct this, it would be necessary to calcine cyanite to at least cone 12 previous to its incorporation into a body mix, but this would involve additional expense. On the other hand the interlocking character of the mullite crystals developed from cyanite indicates a structure possessing possibilities of superior mechanical strength, which might be worth the extra effort involved in its preparation.

Sillimanite shows a smaller expansion than cyanite up to cone 15 and would be subject to the same objections given for that mineral, but not to such a great extent. However, a much higher temperature (probably at least cone 20) would have to be used to convert it into mullite and glass.

In contrast to the behavior of cyanite and sillimanite, andalusite shows only a slight expansion up to cone 15 and its decomposition has been accomplished previous to this point, namely, at cone 13. It should be possible, therefore, to introduce it into a body in the raw state without subsequent production of strains. It would probably be advisable, however, to fire any body containing andalusite above cone 13, if it is desired to convert it into mullite and to absorb incidental strains created at the decomposition point. Bowen and Greig have suggested that owing to the regular structure developed in the breakdown of natural sillimanite where the crystalline phase is external, a body using sillimanite may be mechanically stronger than one using the artificial 1:1 Al_2O_3-SiO_2 mixture where the resulting external phase is liquid. This may also hold good in the case of andalusite; namely, that bodies in which it has been used might be stronger mechanically than those using the artificial 1:1 mixture.

Thus, from the standpoint of changes in volume produced by firing, and the development of artificial mullite, andalusite is the most desirable of the three minerals for use in ceramic ware.

Conclusions

1. Andalusite and cyanite dissociate at high temperatures into mullite and a siliceous glass, both products being the same in optical properties and chemical composition as those resulting from the breakdown of sillimanite as described by Bowen and Greig.

2. Andalusite dissociates at about cone 13, and cyanite at about cone 12. The breakdown in each case is sharp and only extends over a small range in temperature.

3. The microstructures developed in andalusite and cyanite below cone 15 are entirely different and characteristic.

4. Andalusite shows only a slight change in volume at its dissociation point, practically no disintegration or expansion being noticeable even in large fragments. Hence, it may be introduced into a body without previous calcination.

5. Cyanite shows a great increase in volume at its dissociation point accompanied by marked disintegration. This is so pronounced that unless calcined at a minimum of at least cones 12 or 13 previous to its introduction into a body, a weak and porous product would result.

6. Due to the interlocking structure of the crystal areas produced in the breakdown of cyanite, it is possible that cyanite might give a stronger body mechanically than one of the same composition made by using andalusite. Previous calcination, however, would be necessary.

7. Sillimanite can probably be introduced directly into a body with but little disturbance up to cone 20, but in order to convert it into mullite it would be necessary to fire it higher than cone 20. Furthermore, it would be necessary to fire such a body to a still higher temperature in order to produce one of constant volume.

8. Unless cyanite has been previously calcined, andalusite and sillimanite are more desirable because of the great expansion of cyanite at its decomposition point.

9. Between cones 13 and 15, andalusite should be given preference over sillimanite because decomposition has been accomplished and equilibrium established at cone 13.

10. Finally, the value of andalusite lies (*a*) in its dissociation point being at a moderate temperature, (*b*) in the refractoriness of the products of decomposition, (*c*) in the possibilities of great mechanical strength developed by the structure formed in dissociation, and (*d*) in its lack of decided volume change at dissociation.

Acknowledgments

The writer takes this opportunity to express his most sincere thanks to J. A. Jeffery and F. H. Riddle of the Champion Porcelain Company for their hearty coöperation in making the firings; and to E. H. Kraus for suggestions in the revision of the manuscript.

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"BALLING" IN CAST WARE[1]

By W. K. McAfee

ABSTRACT

"Balling" is caused, for the most part, by supply of slip being cut off from a thick section of the ware.

This phenomenon has never caused any appreciable trouble in the casting shops with which I am familiar. I will confine myself, therefore, to a few general observations which may or may not be entirely correct, with the hope of stimulating a lively discussion on the subject.

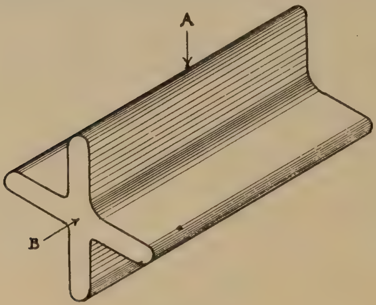

Fig. 1.

We are all familiar with the hair line which shows in the cross section of a piece of green ware that has been solid or double cast. The slip sets up from both plaster surfaces towards the center. The slip shrinks towards these two surfaces, and when the setting-up is complete, there is a noticeable line down the middle. When a supply of liquid slip is not available under a static head during the entire setting-up process, the piece will hollow cast. Even where there is not an appreciable opening on this seam, ware may actually split during firing. This may sometimes be overcome by tapping the mold and causing the two parts to flow together like two drops of water.

Every case of "balling" that has come to my attention occurred in a thick section of ware where the slip was fed through a thinner section, or where a supply of liquid slip was not available to fill up the void during the setting-up period. This may be demonstrated by casting a piece with a cross section in the form of a cross, similar to Fig. 1. If the slip is introduced from one end along the principal center lines through a hole larger than the cross section at the center of the cross, as at "B," there will be no "balling," and the piece will set up solid.

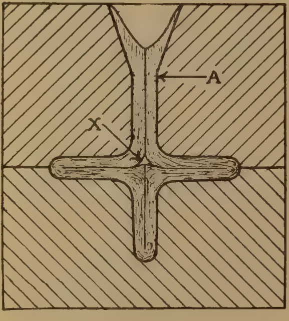

Fig. 2.

If, however, the slip is introduced through one leg of the cross at right angles to the principal center lines, as at "A," this leg will eventually set up solid, cutting off the supply of slip to the center, and evidence of "balling" will be found, as indicated in Fig. 2. The clay particles in packing together move toward the plaster away from the center, and if there is no slip to fill this space there will be a parting, leaving a void, as at "X." The shape and appearance of the opening will depend upon the progress of the setting-up process when the slip is cut off, and probably to some extent, on how much vibration the mold is subject to.

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio. Feb. 1925. (White Ware Division.)

One way to overcome this trouble is to keep thicker sections under a static head of slip. The holes through the plaster pouring funnels should be large enough to prevent their closing up before the piece is entirely set up, or else should be brass lined. A supply of slip should be available for thick sections from an auxiliary funnel if necessary.

A typical example of this method is shown in Fig. 3. In this case, the slip is poured through a brass tube "A" set in the mold and enters through the bottom. This is done to minimize the trapping of air and to prevent the streaking caused by running slip down one side of the mold. The mold fills up allowing the air to pass through the vent funnel "B" in the bottom of the tank (top of the mold). The slip is introduced until it rises in the vent funnel. In case there is not enough slip in the two funnels to counteract the shrinkage, more is poured in both funnels, care being taken to keep the head as nearly equal as possible. The important thing is to keep a positive supply of slip available, until it is certain the ware is set up solid.

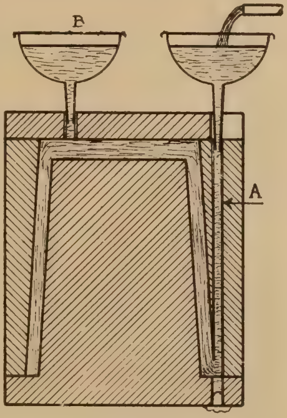

Fig. 3.

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STUDY OF SEGREGATION IN PORCELAIN FILTER CAKE BY PETROGRAPHIC METHODS[1]

By Louis Navias

ABSTRACT

The segregation which takes place in a filter cake of a porcelain mixture has been studied in thin sections made from slices of the filter cake fired to cone 10. A lenticular segregation is illustrated by photomicrographs.

Of prime importance in the ceramic industry is a homogeneously mixed composition. To obtain such a condition in the fluid state mixing, blunging and grinding are resorted to, and in the plastic state wedging by hand, kneading and pugging by machines are common methods.

The filter press in the act of dewatering the mixture, however, often partially destroys the homogeneity obtained in the initial processes, by causing a segregation of the constituents in the filter cake. There is no need of stressing the importance of this point and of the necessity of making a uniform filter cake, irrespective of the mixing that takes place in the plastic condition. The present note does not contain a panacea for curing or preventing the segregation of the constituents during filter pressing, but merely a visual demonstration of the segregation to reveal its structure. The customary petrographic methods of making and studying thin sections were employed.

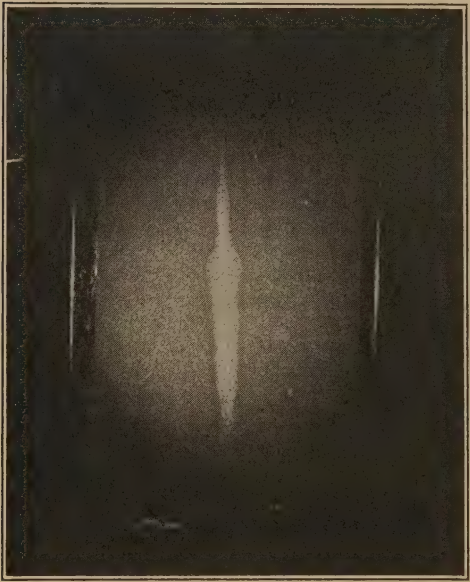

Fig. 1.—Magnification $1^1/_2$ × ordinary light. Thin section of segregated porcelain filter cake.

A filter cake having decided segregation can often be separated into two leaves by merely pulling it apart at the middle of an edge. The contact surfaces of the two halves are usually sandy, that is, gritty, coarse grained and devoid of clay and hence plasticity. Slices of such filter cakes, cut to give a cross section of the cake, when dried and fired give an indelible record of the distribution of the constituents contained in them.

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb., 1925. (White Ware Division.)

Our Observations

Slices of a porcelain mixture fired to cone 10 contained segregation in the form of a series of double convex lenses laid end to end and separated by connecting thin strips of segregated material. The uniformly spaced lenses or heavy deposits are suggestive of Liesegang's rings, indicative of rhythmic or pulsating deposition. In cutting through the filter cake the major part of the mass yielded a smooth surface whereas the segregated portion gave an uneven and ragged surface.

A thin section of a rather distorted but complete lens segregation was made and photographed by ordinary light. It is shown in Fig. 1, the magnification being $1^1/_2$ diameters. Around the central core a fine band is noticeable, separating the lens from the main portion of the section. The lens is noticeably more transparent than the remainder of the section. When magnified to 16 diameters the central portion takes on a different appearance. Figure 2 was taken with ordinary light, and *c* represents the lenticular central segregation, *b* the fine band referred to above, and *a* the main portion of the filter cake.

Figures 3 and 4 taken with polarized light and magnifications of 63 and 100 diameters, respectively, show one half of the cross section, the letters referring to the same zones as in Fig. 2. The white particles are quartz grains. Descriptions of the separate zones are as follows:

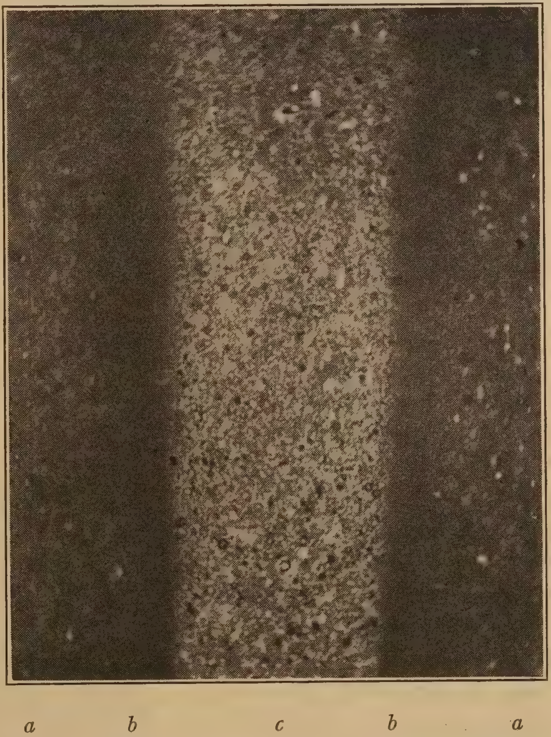

FIG. 2.—Magnification 16 × ordinary light. Thin section of segregated porcelain filter cake.

Zone *c*. The main segregated area or lens contains large particles of quartz imbedded in a feldspar glass, the latter being the cause of the transparency. As under higher magnifications no large flakes or areas of of clay are found, it is evident that the segregation consists mainly of quartz and feldspar.

Zone *b*. The thin bands *b*, flanking the central area *c* are found to consist of clay in a fine state of subdivision, almost exclusively. The quartz particles are few in number and very small in size. The bands are less transparent and translucent than zones *c* and *a*.

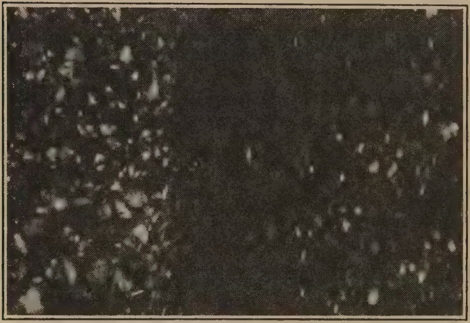

FIG. 3.—Magnification 63 × polarized light. Thin section of segregated porcelain filter cake.

Zone *a*. These large areas compose the bulk of the filter cake. The appearance is that of the ordinary porcelain with quartz and clay particles well distributed. The quartz grains are not as large as those in zone *c*, nor packed as closely. The clay lakes show the development of mullite quite plainly.

AVERAGE DIMENSIONS OF QUARTZ GRAINS

Zone *c*	0.0035—0.0070 cm.
Zone *b*	0.0007—0.0014 cm.
Zone *a*	0.0018—0.0035 cm.

Another filter press yielded filter cakes from which slices were obtained having segregated areas of rather uniform width, except at the tip of each slice, corresponding to the periphery of the cake, where a large lens was formed. The lens was more complicated in its structure than the one described above, for it contained two extra zones of segregation on each side of the central coarse zone. Using the symbols of the photographs and starting with the central coarse zone, the formation to either side was *c*, *b*, *c*, *b*, *a*. The elongated quartz particles in the clay zones *b* and in their vicinity were noticeably oriented, having their long sides parallel to the direction of segregation in the section.

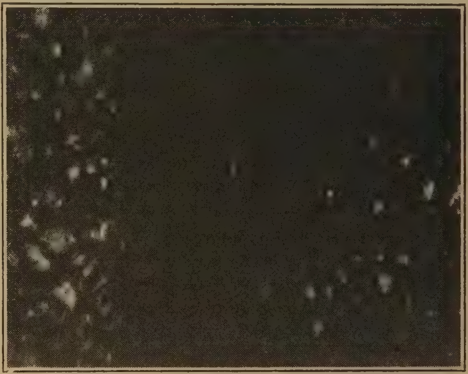

FIG. 4.—Magnification 100 × polarized light. Thin section of segregated porcelain filter cake.

An average width for each of the zones may be of interest, *c* 0.12 cm., *b* 0.038 cm. and *a* 1.25 cms. Hence the total widths of the segregated areas across a filter cake are *c* 0.12 cm., *b* 0.076 cm. and *a* 2.5 cms. A rough calculation shows that of approximately 7.5% of material segregated, zone *c* contains 4.5% and zone *b* 3%.

In conclusion it is hoped that this application of an old method will prove useful in determining the best procedure for filter pressing by following the concurrent changes in segregation delineated in the fired slices.

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Discussion

F. H. RIDDLE: We can open our discussion with the relative merits of diaphragm pumps, plunger pumps and compressed air for filter pressing and methods of pugging. I know one plant where compressed air is used in place of the ordinary filter pump and then the material is pre-pugged before it goes to storage. After it comes from storage it is pugged twice and sometimes three times in order to get away from some of the troubles.

There is a tendency on the part of most of the potters to do more instead of less work in trying to get a uniform cross-section, not for the filter cake, although that has worked, of course, but to the final column that goes to the forming benches.

F. V. DRAKE: There is one process where they have introduced a four-cylinder pump in place of the two-cylinder pump, and in that manner there is no chance at all for settling between the strokes of the pump. It keeps everything in suspension the entire time and this has minimized segregation.

W. W. McDANEL: We had this trouble in its worst form. We doubled the length of the press and cut the pressure from eighty pounds to forty-five pounds. This gave us a good firm and homogeneous cake. We were of the opinion that the high pressure drove the finer particles to the surface, while the coarse particles, being unable to retain their proper place in the mix, were left in the center. No amount of pugging could restore the plasticity lost by the separation. We were surprised to find our press delivering twice as much clay in the same time, requiring exactly the same time to pump as with the high pressure.

H. GOODWIN: If the agitators are not started a sufficient length of time before the pump is started to work there will be segregation. This has a bearing on the structure as well as the pump. We should take lack of homogeneity in the agitator into consideration as one of the causes of segregation in the filter cake. Probably we should consider grinding the materials before they are put into the agitators. There are many varieties of pumps, but we do not know what is the best to adopt.

F. H. Riddle: Mr. Goodwin's point about grinding is good. If we are troubled with a separation of fine and coarse particles, we must eliminate the coarse particles by finer grinding.

R. M. King: Was the material prepared in a blunger or in a ball mill?

L. Navias: The body was only blunged, or rather one body was blunged and the second body was ground, the latter in a plant where they grind the body some three hours, I believe.

R. M. King: Did you find any difference in the segregation?

L. Navias: No. The segregated particles were smaller in the second case, but they conform somewhat to the figures given; that is, the maximum values were lower, but the general appearance and the general segregation was similar in both cases.

R. M. King: What was the percentage of ball clay?

L. Navias: About 25%.

S. J. McDowell: At what pressure were those compressors pumped?

L. Navias: In the case illustrated about 60 to 70 pounds.

S. J. McDowell: Dr. Navias' paper is a very interesting and graphic portrayal of filter press segregation.

One of the causes of this segregation is the presence of settled non-plastic material on the bottom of the cisterns. Emptying and thoroughly washing of the cisterns at frequent and definite intervals is a great aid in the alleviation of this lens structure in the filter press cake.

Where the non-plastic material has a high specific gravity, this is particularly true.

F. H. Riddle: These details are important and there are other points of interest. How coarse are the coarse particles in your first leaf, and how are they in the last leaf? It would be interesting to try filter pressing materials where you have two different specific gravities. For example, a sillimanite with a specific gravity of over 3 and the rest of the material about 2.6.

H. Goodwin: It would be of value if we had the time taken to fill the presses, size of the presses and character of the pump.

SOME NOTES ON THE COLOR OF ANTIMONY ENAMELS[1]

By M. E. Manson

ABSTRACT

Pure white antimony oxide does not give as good a color or opacity in enamel as the gray, impure, domestic product. The better color and opacity of enamels made with the latter is probably due to the impurities contained in the antimony.

Introduction

Both Staley[2] and Shaw[3] have discussed the question of color control in antimony enamels but neither specified the source of the antimony oxide used in their experiments. The results of an investigation of mine lead me to believe that this is an important point in any discussion of this subject.

A few years ago there was an enamel in use at our plant, which derived its opacity from a mixture of tin and antimony oxides smelted into the frit. The odd thing about the formula was the extremely low percentage of opacifier used, in spite of which the opacity of the enamel was very good. The enamel was of the high head type and contained less than 5% total tin oxide plus antimony oxide. The tin was present in such a small amount that it must have been completely dissolved in the frit, producing no opacity whatever. What there was, evidently came from the small amount of antimony oxide present, plus the fluoride capacity.

The particular antimony used in this enamel was a domestic oxide. I believe there is only one domestic source for this material. Since the purchasing department did not wish to be confined to one company on any material, we tried, at various times, to substitute Chinese oxide, supplied by various companies. Every such attempt was a failure, the resultant enamel being a decided blue white of low opacity, instead of its usual opaque cream color. This was the more strange because the domestic oxide was a very impure product containing only about 92% oxides of antimony and varying in color between light gray and slate gray while the Chinese oxide was pure white and contained about 98% of the oxides. The problem presented therefore was to find if possible some way to get the same results with pure antimony oxide as with impure.

Chemically there are three oxides of antimony, represented by the formulas, Sb_2O_3, Sb_2O_4, Sb_2O_5. I believe the ordinary commercial product, while it contains all of these oxides in varying amounts, consists principally of the trioxide. There is probably a difference in the opacifying power of the three oxides, increasing as the degree of oxidation increases, although I know of no work done to prove this. Unfortunately, I have been unable to find any methods of analysis of antimony which allow the quantitative determination of these three oxides. Since all three oxides are present in the commercial oxide, it is impossible to determine the per cent of metallic antimony present and calculate from that the per cent of oxide.

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio. (Enamel Division.)

[2] Bur. Stand., *Tech. Paper* **142.**

[3] *Ibid.,* **165.**

All three oxides are however soluble in hot concentrated hydrochloric acid, so that by determining acid insoluble, water soluble, and iron and sulphur in the acid soluble material, the total antimony oxides can be determined fairly well by difference.

The Investigation

In the following experiments, two kinds of material were used. One, a Chinese oxide, called "C" hereafter, contained 98% antimony oxides, 1.5% water soluble material and 0.5% acid insoluble. The other, a domestic oxide, called "S" hereafter, contained 91% antimony oxides, 7% acid insoluble, 1.5% water soluble and the remaining 0.5% consisted of iron and sulphur. The sulphur is from unoxidized Stibnite. All smelts were made in Battersea crucibles in the laboratory. The parts of materials used were equivalent to pounds in the factory smelter. A smelt of our regular enamel using "S" antimony was made first as a standard.

SERIES I—Effect of varying amount of antimony oxide. It was possible that, being so much purer, less of the "C" oxide should be used or that, being of a different physical structure, it was more readily dissolved in the frit, and more should be used.

Test 1—Standard formula without change, using eleven parts antimony. An enamel with a blue green tint and poor opacity was obtained.

Test 2—Nine parts antimony—no other change. Result the same as Number 1.

Test 3—Five parts antimony. Same color as 1, slightly poorer opacity.

Test 4—Eighteen parts antimony. Same color as 1, but with slightly better opacity.

SERIES II—Effect of omitting tin oxide. Enamelers have noticed that when tin oxide and antimony oxide are smelted together in the same frit, a blue color results. "C" oxide used.

Test 5—Fifteen parts antimony, no tin. Enamel was greener than 1.

SERIES III—Effect of varying calcium content. Staley in a series of experiments showed that when both antimony and lead oxides were present in an enamel, a brown coloration was produced. The addition of calcium either as fluorspar or whiting produced a blue color which neutralized the brown. Therefore in this case, we might expect to lessen the blue color by reducing calcium. The usual eleven parts of "C" antimony were used.

Test 6—Seven parts of whiting were cut out and in its place two parts borax and four parts soda ash added. Resulting enamel was about the same as No. 1.

Test 7—Fourteen parts of fluorspar removed and sodium fluoride substituted. This gave a very yellow enamel, entirely different in color from No. 1, yellower than the standard.

Test 8—Seven parts of fluorspar removed and sodium fluoride substituted. This enamel was not so yellow as Test 7, but yellower than the standard.

Evidently calcium, at least as fluorspar, affects the color, but no change in fluorspar was sufficient to produce the opaque cream color of the standard. Test 11 was too blue, but Test 8 was too yellow, and neither sample showed the required opacity.

SERIES IV—Effect of increasing sodium nitrate. It is possible that the Chinese oxide contains considerably more Sb_2O_3 and less Sb_2O_5 than the domestic product. Therefore an increase in the oxidizing effect during smelting might help.

Test 9—The sodium nitrate was increased from 16 to 21 parts, while a reduction in soda ash kept the Na_2O content the same. The resultant enamel was bluer than the standard but not as blue as Test 1. Opacity poor.

At the time these tests were performed, I went no further along this line. It seemed possible that a large increase in sodium nitrate might have produced a cream white, but the resultant enamel would have probably had so much soda in it that its luster and workability would have been impaired.

SERIES V—Effect of small amounts of impurities. Since our best results were obtained with an impure oxide, it seemed possible that some of the impurities might be the cause of the good color and opacity. The standard formula called for eleven parts of domestic antimony. The amounts of various impurities added to the batch by this antimony were calculated, and were then added to batches made of "C" oxide.

Test 10—Regular formula plus 0.2 part of sulphur. This enamel was very green.

Test 11—Regular formula plus 0.5 part iron sulphide. Same result as Test 10.

Test 12—Regular formula plus 0.5 part manganese dioxide. Enamel slightly greener than Test 1.

Test 13—Regular formula plus 0.4 part iron oxide. Enamel had same appearance as Test 12.

Test 14—A large amount of our domestic oxide was dissolved in concentrated hydrochloric acid, filtered, and a quantity of the acid insoluble material obtained. This was tan colored, and analysis revealed a siliceous material containing about 60% SiO_2. No attempt was made at a complete analysis. A smelt was made of the regular formula plus 0.7 part acid insoluble. The resultant enamel had a brown tint, browner than the standard. A fair enamel.

Test 15—Regular formula plus 0.5 part acid insoluble. Enamel was greenish.

Test 16—Regular formula plus 0.9 part of acid insoluble. Enamel was too brown.

The above series showed that the insoluble material in the domestic antimony exercised a decided effect on the color of enamel. Test 14 was the closest approach to the standard of any of the tests, but it still left much to be desired. Knowing that different shipments of this antimony varied between 5 and 10% of this material, it is easy to understand why different lots of antimony give different colored enamels.

SERIES VI—

Test 17—Regular formula, using a French process antimony oxide over 99% pure. The enamel was exactly like Test 1 blue.

Conclusion

The above experiments convinced us that we could use only one kind of antimony oxide in our formula. We still cannot say definitely what causes the difference in the color produced by the impure domestic oxide and the relatively pure Chinese oxide. The solution may lie in colloid chemistry. In 1923, in an article entitled "The Industrial Outlook for Colloid Chemistry" by H. N. Holmes,[1] he made the following statement:

"Since ions exist in melted salts there is a possibility that certain ions in a melted glass or enamel may peptize a pigment added to the melt. The composition of enamels might be changed so as to introduce desirable ions or even protective colloid material. Coagulation by ions may also merit study in such systems."

Rundle Mfg. Co.
Milwaukee, Wis.

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[1] *Jour. Ind. Eng. Chem.*, **15**, 857 (1923).

THE LABORATORY TESTING OF PLASTIC REFRACTORIES[1]

By R. F. Geller and W. L. Pendergast

ABSTRACT

Twelve brands of plastic refractories, representing the products of nine manufacturers, were subjected to standard and modified laboratory tests for high grade refractories. The data obtained show the chemical and physical characteristics of the material now furnished to the trade and indicate the results which may be expected from a technical examination of this type of product.

Introduction

Composition

The product referred to in this paper as a "plastic refractory," a name now fairly familiar to the trade, is composed essentially of grog, raw clay and sufficient water to render the mass plastic or of a "stiff mud" consistency. The grog consists principally, if not entirely, of calcined clay,[2] and comprises from 50 to 75% of the total solid material. The raw clay is used to supply the necessary bond, the percentage required depending on its plasticity; *i. e.*, as the manufacturer would aptly express it, not more than enough of the raw or plastic clay is added to "carry" the grog, in order to prevent excessive shrinkage in drying and firing.

Use

While a plastic refractory was put on the market twenty years ago, under the proprietary name of Plastic Fire Brick, its use was limited until about 1912. Since then it has met with a constantly increasing demand so that at the present time the total production has been estimated as exceeding 100 tons per day. Approximately 75% of the total present output is used for special shapes, repairs, doors, arches, walls, etc., in power plants, but the material is being adapted to construction and repair work in practically every type of heat installation from a baker's oven to the boiler setting of a navy destroyer.

Purpose of Investigation

Because of the increasing demand for plastic refractories, it is logical to assume that the number of brands and varieties being placed on the market, together with the volume of purchases, will necessitate a specification for this commodity. In fact, the American Marine Standards Committee is at this time engaged in developing such a specification. The present investigation of the physical and chemical properties of plastic refractories, and of their behavior in laboratory tests, was undertaken to aid in the development of such specifications, and also to help the manufacturer and consumer to a better understanding of the material.

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb., 1925. (Refractories Division.) Published by permission of the Director, Bureau of Standards.

[2] It is customary in most cases to add ganister, in an endeavor to overcome the shrinkage natural to clay on heating.

Coöperation The investigation was carried out in coöperation with the Navy Department. Complying with a request from this laboratory, samples were submitted by Louisville Fire Brick Works, S. Obermayer Co., Crescent Refractories Co., Cornish Co., Laclede-Christy Clay Products Co., Seaboard Refractories Co., Jointless Fire Brick Co., Denver Fire Clay Co., A. P. Green Fire Brick Co.

Scope of Investigation

These samples were tested to determine the water content as received, softening point, dried modulus of rupture and shrinkage, fired shrinkage and absorption, resistance to spalling, resistance to deformation at high temperatures, chemical composition, and fineness.

The results obtained by the Bureau were correlated and also compared with results of test determinations submitted by the Navy Department and by the manufacturers.

Method of Testing

All of the specimens were prepared by ramming into molds with a wooden mallet.

The water content, dried shrinkage and fired shrinkage are expressed in percentage of plastic weight and length, respectively.

Modulus of rupture was determined with an Olsen testing machine, over a 7-inch span, on 3 x 3 x 10-inch specimens.

Fineness was determined by screen analyses, using the wet method and U. S. Standard sieves.

The chemical analysis made by the Bureau consisted of the routine determination of SiO_2, Al_2O_3, Fe_2O_3 and TiO_2. Other constituents were not determined, but the difference between 100% (non-volatile) and the sum of the constituents determined was regarded as the percentage of alkalis.

The softening points were determined in an electrically heated muffle,[1] and measured by means of Orton pyrometric cones. The heating schedule followed is that prescribed in the A.S.T.M. Standard Method of Test for Softening Point, Serial Designation C 24–20.

The quenching test was conducted on 3 x 3 x 10-inch specimens which had been fired at 1400°C for five hours, following the method described in a "Progress Report on Specifications for Refractories."[2]

Absorption is expressed in percentage of dry weight.

In the endurance test, specimens averaging 10 x 4.7 x 2.7 inches, made in a brick mold and fired for 5 hours at 1400°C, were refired for 72 hours at 1450°C. For shrinkage and absorption determinations the specimens were fired on end under no load, and for the determination of resistance to deformation the specimens were laid flat over a 7-inch clear span, and loaded at the center with a brick cut to weigh 6 pounds.[1] The deflection was measured after the specimens had cooled.

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[1] W. L. Pendergast, "Electric Furnace for Softening Point Determinations," *Jour. Amer. Ceram. Soc.*, **8** [5], 319 (1925).

[2] *Jour. Amer. Ceram. Soc.*, **6** [10], 1098 (1923).

Results

The data obtained from these tests are either given in Table I or shown in Figs. 1, 2 and 3.

Water Content The water content of the specimens as received (by this is meant the water which is lost on drying to constant weight at 110°C and generally referred to as "shrinkage and pore water") varied from 9.3 to 15.7% (Table I). Considering the possibilities of error in the determination, as well as variations which can reasonably be expected in the material itself, it is concluded that the water content of the samples examined was practically the same for all and would average 12%.

Dried Shrinkage The linear shrinkage during air-drying averaged 1.5% and, with the exception of Brand No. 1, the maximum deviation from this average did not exceed 0.6%. As in the case of the water content, a consideration of the probable error in measurements and the variations in the material itself seems to justify the statement that the drying shrinkage was practically the same for all materials submitted.

Modulus of Rupture, Dried The dry strength of a material which is not subjected to handling in that state is probably not an important factor. This is particularly true in those cases where the plastic mass is used for patching, to replace special shapes around burner ports, at the top of walls in marine boilers, and similar purposes resulting in a product which is fairly compact in shape and not subjected to superimposed loads. Nevertheless, and this is particularly true of monolithic wall construction, the strains incident to contraction and expansion of various parts of a boiler setting or similar installation, during the drying and preliminary heating of the plastic, are quite likely to cause cracking and the consequent lowering of life in service. It would, therefore, appear advisable to manufacture a product of the highest possible dried strength consistent with the maintenance of refractoriness, and low drying and firing shrinkage. This appears to have been done in the case of Brands 8 and 9 which show a strength approximately double that of the other brands, although the shrinkage is not excessive (Table I). Tests indicate that this high strength was not due to

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[1] This is approximately equivalent to loading a brick of $4^1/_2$ x $2^1/_2$ inch cross section, laid flat over a 7-inch span, with a brick cut to weigh 5 pounds.

Free Public Library. Newark, N.J.

TABLE I

					After firing for 5 hours at 1400°C			Endurance test, 72 hours at 1450°C				
Laboratory number of brand	Per cent water content as received	Cone softening point	Per cent linear drying shrinkage	Lbs. / sq. in. modulus of rupture, dried	Per cent shrinkage, linear	Per cent absorption	Number of quenchings required to produce failure	Inches deflection when transversely loaded	Per cent linear shrinkage	Per cent absorption	No. of quenchings required to produce failure (1550°C/48 hrs.)	Navy Simulated Service Test
1	14.3	31	2.7	54	3.4	11.5	27	5/32	4.3	8.9	..	Passed
2	10.4	32	1.2	33	4.5	9.4	50	8/32	4.8	7.5	..	Passed
3A	13.2	31	1.0	34	5.5	9.9	36	4/32	11.6	8.2	..	Passed
3B	13.4	31	0.9	54	3.9	8.1	39	3/32	9.1	6.9	..	Not tested
3C	9.3	32	2.1	53	7.4	7.5	40	4/32	13.3	4.6	..	Not tested
4	11.9	32	1.6	57	3.2	9.2	46	6/32	5.6	7.3	..	Passed
5	11.7	32+	1.1	46	3.6	10.2	19	4/32	7.5	8.5	..	Failed
6	15.7	30	0.9	27	3.8	15.3	15	11/32	12.5	9.0	..	Failed
7	11.4	32	1.5	52	1.2	12.6	16	3/32	0.3	9.9	12	Passed
8	12.2	32	2.0	101	1.9	13.2	15	9/32	2.6	10.1	5	Passed
9	13.6	34	1.9	111	3.2	13.5	15	3/32	5.5	10.7	41	Not tested
10	9.9	32	1.5	76	2.5	9.2	20	7/32	2.5	7.3	..	Failed

the use of sodium silicate but to the nature of the clay bond, either natural or developed by weathering or other means, which is in accord with statements from manufacturers that sodium silicate is not being used in any plastic refractories.

With the exception of the two brands discussed, the dried strength of the various plastic refractories is fairly uniform, averaging 48.6 pounds per square inch and varying generally from 33 to 57 pounds per square inch (Brands 6 and 10 reached a minimum of 27 and a maximum of 76 pounds per square inch, respectively). That these exceptions may not be of significance is indicated by the fact that both failed in the Navy Simulated Service Test (Fig. 4).

Screen Analyses The data obtained by means of screen analyses are shown in Fig. 1.

Since clay matter, of which plastic or bond clays are almost entirely composed, will readily pass a 200-mesh screen, and calcined clay and ganister is not ground to this degree of fineness in practice, it was assumed that the 200-mesh screen would roughly separate the grog from the bond. Based on this assumption the screen analyses indicate that all of the plastic refractories tested contained from 32 to 47% bonding material, or an average of 40%. It is realized that the screen analyses may indicate a lower percentage of bond clay than is actually present in those mixes containing a flint or a semi-flint clay which has only partly slaked down.

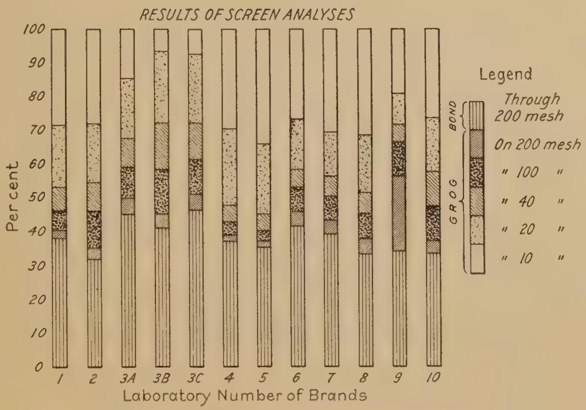

FIG. 1.

The composition of the grog, as regards fineness, varied over a rather wide range. This is particularly true of the portion remaining on the 10-mesh screen. (For Brand No. 5 this constitutes nearly 35% of the dry body, and for Brand No. 3B not quite 7%.) In addition, that portion passing the 10-mesh and remaining on the 20-mesh screen varied from 9 to 22%, the portion through 20- and on 40-mesh from 4 to 13%, the portion through 40- and on 100-mesh from 3 to 13%, and the portion through 100- and on 200-mesh from 2 to 22%.

There is no relation evident between these variations in sizing and the behavior of the materials in other tests.

Chemical Composition

The results of chemical analyses are shown in Figs. 2 and 3.

As a result of the investigations of clay fire brick previously referred to, it was found advisable to designate those refractories containing more than 20% uncombined quartz (Fig. 3) as siliceous. Accordingly, Brand No. 6 should be classed as a siliceous plastic, and it is one of rather high grade since it had a softening point equal to that of Orton pyrometric cone No. 30 and withstood 15 quenchings without failure.

With the exception of this Brand (No. 6) the chemical analyses (and the rational compositions calculated from them) indicate that all the materials tested have compositions within the range characteristic of the so-called high grade clay refractories, *i. e.*, the SiO_2 varies from 40 to 65%, the Al_2O_3 from 30 to 50%, and the total flux from 3 to 6%.

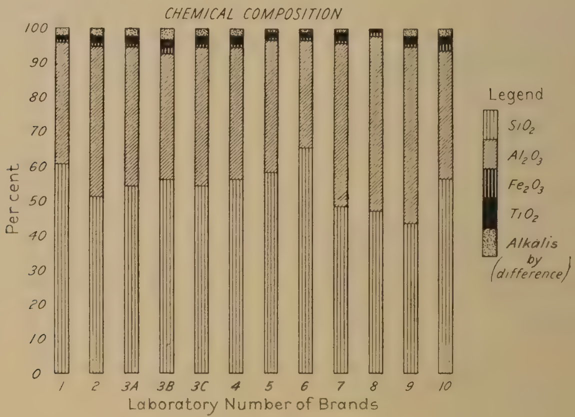

FIG. 2.

Petrographic Examinations

The work of the chemical laboratory was supplemented by petrographic examinations. These examinations not only checked, for example, the evident high uncombined quartz content of Brand No. 6, but also show that Brands 7 and 8 contained ganister (uncombined quartz) and diaspore, which is not evident from the chemical analyses on account of the relatively high Al_2O_3 content of diaspore.

Softening Points

The softening points (with the exception of Brand No. 6 discussed above) range from that of cone 31 to that of cone 34 (Table I), or approximately from 1650° to 1710°C. No discussion of these data is required other than they check the conclusion, based on the chemical composition, that the materials tested are of the same general quality as high grade clay refractories.

Resistance to Spalling The resistance to spalling, as indicated by the number of quenchings from 850°C to running water required to produce failure, varied considerably (Table I). As would be expected, Brand 6 (containing considerable quartz) withstood the least number of quenchings.

That Brands 7, 8 and 9 did not show greater resistance is not so readily explained by the chemical composition, but may be explained by considering the results of the petrographic examination which indicated that the grog was composed of ganister and calcined diaspore. Ganister, as is well known, continues to expand at high temperatures, due to molecular changes. Diaspore, on the other hand, continues to shrink during use because ordinary calcining temperatures are not high enough to bring about appreciable vitrification. This alone might induce strain sufficient to lower its resistance to spalling. Also, diaspore itself when used as a refractory will often fail in service through spalling; whether this is due to the continued shrinking already mentioned, high modulus of elasticity in shear together with a low shearing strength, low diffusivity,[1] low tensile strength (or a combination of these) has not been definitely determined. In any case, one would assume that the resistance to quenching could be increased by bringing the diaspore-ganister mixture to a more stable and mechanically stronger form through higher initial firing, which probably explains why Brands 7 and 9 passed the Navy Simulated Service Test. In this test,[2] the refractory is heated for 24 hours at 1590°C (approximately 2895°F) before being rapidly cooled.

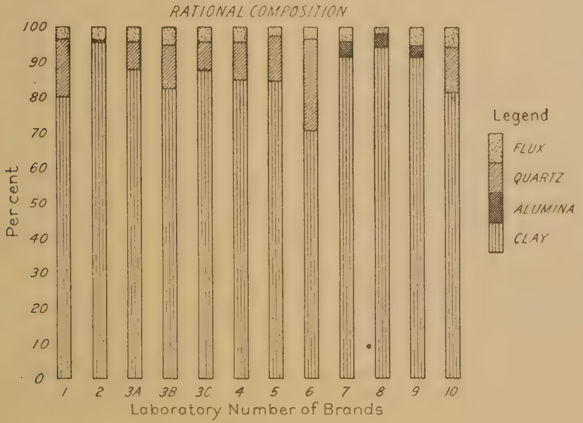

FIG. 3.

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[1] F. H. Norton, *Jour. Amer. Ceram. Soc.*, 8 [1], 29 (1925).

[2] For a description of the test see the U. S. Government Master Specification for Fire Clay Brick, Federal Specifications Board Specification No. 268.

In an endeavor to verify this assumption, five specimens of each of Brands 7, 8 and 9 were fired at 1550°C for 48 hours (cone 23 flat); cooled in the kiln and quenched as before from 850°C. The results are given in Table I and Fig. 4. It is evident that higher firing materially increased resistance to spalling for Brand 9 containing no ganister, but lowered the resistance for Brands 7 and 8 containing ganister.

Fired Shrinkage and Absorption

Although the shrinkage, both after firing at 1400° and 1450°C (Table I), bears no consistent relation to results obtained with other tests, it is a property of plastic refractories which no doubt deserves serious consideration by the manufacturer. As the data show, it varied after the higher firing (1450°C) from less than 1% to nearly 14%. Since the results of the quenching test indicated that a ganister content of less than 20% did not seriously affect resistance to spalling, it would appear desirable to use that proportion of ganister (not exceeding 20%) which would produce the least fired shrinkage of the product. It is more advisable, however, to obtain the same result by proper grading and proportioning of the grog, and adjustment of the grog-bond ratio, if the raw materials at hand permit.

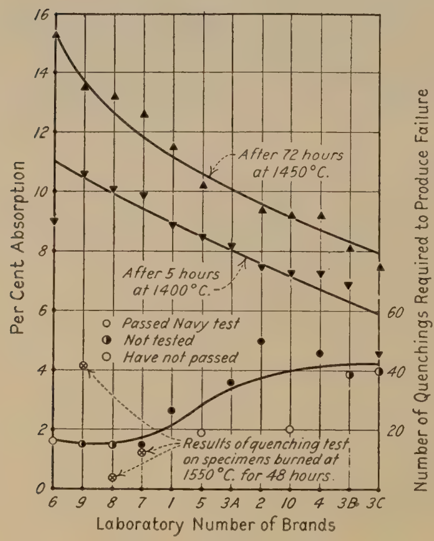

FIG. 4.

Relation of Resistance to Spalling and Absorption to Results in Navy Test

A relation between the results of absorption, resistance to spalling and simulated service tests is indicated by the data and emphasized by means of Fig. 4. While no data are available for Brands 3B, 3C and 9, it is assumed, from their similarity to Brands 3A and 8, that they would pass the Navy test. Brands 5, 6 and 10 did not pass the Navy test.

Based on the assumption just made regarding Brands 3B, 3C and 9, the data show that all plastics which withstand more than 25 quenchings would pass the Navy test while, of those withstanding less than 25 quenchings, only the high alumina materials would pass the test. The effect, if any, of absorption is not clearly indicated, but the data are given in Fig. 4 for the convenience of the reader. Further tests may demonstrate

TABLE II

COMPARATIVE DATA ON CHEMICAL COMPOSITION AND SOFTENING POINT DETERMINATION

Lab. no. of brand	Source of data[1]	Per cent SiO_2	Per cent Al_2O_3	Per cent Fe_2O_3	Per cent TiO_2	Per cent alkalis by difference	Softening point, cone
1	A	55.3	39.8	1.2	2.2	1.5	31
	B	60.6	35.2	0.6	1.4	2.2	31
	C	58.2	36.2	0.4	1.7	3.5	30–31
2	A	51.2	44.3	1.4	1.2	1.9[2]	...
	B	51.6	43.8	1.1	1.8	1.7	32
	C	51.2	44.3	1.6	1.2	1.7	30–31
3A	A	....	....	...	...	...	...
	B	55.0	39.6	1.4	1.8	2.2	31
	C	52.9	43.5	0.5	1.3	1.8	32
3B	A	57.2	38.1	1.8	1.2	1.7	...
	B	57.5	36.7	1.6	1.8	2.4	31
	C	....	....	...	...	...	...
3C	A	53.6	41.6	2.0	1.6	1.2	...
	B	55.4	39.5	1.4	1.9	1.8	32
	C	....	....	...	...	...	...
4	A	....	....	...	...	...	...
	B	56.7	38.1	1.2	1.8	2.2	32
	C	56.3	39.6	0.5	2.3	1.3	30–31
5	A	60.0	38.0	...	...	...	33
	B	59.0	37.9	1.2	1.2	0.7	32–33
	C	62.1	33.9	0.5	2.2	1.3	32
6	A	57.1	38.6	1.6	2.4	0.3	...
	B	65.6	30.9	1.0	1.4	1.1	30
	C	....	....	...	...	...	...
7	A	....	....	...	...	...	...
	B	48.7	46.7	1.3	1.8	1.5	32
	C	49.4	42.0	3.8	3.7	1.1	31–32
10	A	....	....	...	...	...	...
	B	57.3	36.4	1.9	2.0	2.4	32
	C	49.2	38.0	8.7	2.5	1.6	31

[1] A—Submitted by manufacturer. B—Obtained by Bureau of Standards. C—Submitted by Navy Department.

[2] Probably obtained from Navy Department.

that comparatively high absorption is not desirable in material of this type, as was shown for fire clay brick.[1]

Deformation under Load

The resistance to deformation (determined as described under Endurance Test) was uniformly low, ranging from $^{3}/_{32}$ to $^{11}/_{32}$ inch and averaging $^{6}/_{32}$, which compared favorably with so-called No. 1 fire clay brick.[4]

Comparison of Data from Three Laboratories

As a result of increasing interest in controlling the quality of ceramic products by means of laboratory tests, and the consequent adoption of such tests by many plants and research laboratories, the question arises as to the relative accuracy of data obtained by independent investigators.

The information obtained in the course of this work affords an unusual opportunity to present data on chemical compositions and softening points from three sources. These data are given in Table II and, as noted there, were obtained by the manufacturer, the Navy Department and the Bureau of Standards. They indicate that differences of $^{1}/_{2}$ to 1 cone can be expected in softening point determinations and that the analyses for a single constituent may vary, generally, from 0.1 to 2.0%, although variations of over 5.0% were noted.

It should be borne in mind that these data on chemical compositions are presented neither in a spirit of criticism nor for the purpose of placing the cause for such variations as may exist due to lack of uniformity in the product, precision in analytical methods, or sampling. The fact is that data of this character are being used, by different investigators, as representing a certain material. Although variations obtained by three different laboratories do not necessarily vitiate the value of the results as a basis for interpretation, they are far too great to overlook. Also, it is hardly fair to the manufacturer to conclude that the product varies as much as indicated by these results but it is evident that a combination of variations in product, methods of sampling, and testing used by different investigators have produced the differences noted. In order then to obtain a better basis for comparisons it seems imperative that methods for sampling and testing must be clearly defined.

Conclusions

The outstanding result obtained in this work is the indication that plastic clay refractories, as now manufactured and as typified by the brands tested, are inherently the equal of the so-called highest grade refractory clay brick and are more uniform in composition and quality than that group of brick which are on the market as being of No. 1 refractory quality.

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[1] *Loc. cit.*

The general conclusion just stated is based on the following experimental results:

1. The water content varies from 9.3 to 15.7 %, averaging 12%.

2. The drying shrinkage was practically uniform, averaging 1.5%.

3. The dry modulus of rupture varied generally from 33 to 57 pounds per square inch, although a minimum of 27 pounds and a maximum of 111 pounds per square inch were noted. The average was 48.6 pounds per square inch.

4. Screen analyses indicate that the materials average 60% grog and 40% plastic clay. The sizing of the grog varied over wide ranges, but had no noticeable effect on the other properties of the product.

5. The SiO_2 content varied from 43.8 to 65.6%, the Al_2O_3 from 30.9 to 50.8%, Fe_2O_3 from 0.6 to 1.9%, TiO_2 from 0.2 to 2.3%, and alkalis (by difference) from 0.2 to 2.4%.

6. The softening points ranged from that of cone 30 to that of cone 34.

7. Resistance to spalling was uniformly high, from 15 to 50 quenchings being required to produce failure.

8. The specimens, when transversely loaded in the endurance test, showed deflections averaging from $^3/_{32}$ to $^{11}/_{32}$ inches, the average being $^6/_{32}$.

The data also indicate: (*a*) that brick of high resistance to spalling and low absorption (within the range for the materials tested) show better resistance to failure in the Navy Simulated Service Test; and (*b*) that a variation of from $^1/_2$ to 1 cone in softening point determinations and, generally, from 0.1 to 2.0% on each constituent in chemical analyses can be expected for different samples representing one brand or product when tested in different laboratories.

METHODS AND MANUFACTURE OF SEWER PIPE IN CANADA[1]

By Charles A. Millar

ABSTRACT

Description of clays used and methods employed in production of sewer pipe in Canada.

History

The manufacture of Sewer Pipe in Canada dates back to about 1860. About that time a small factory was established in the City of Hamilton and continued up to the present time, now under the name of the Toronto and Hamilton Sewer Pipe Co., Ltd. The Ontario Sewer Pipe and Clay Products Co., Mimico, was founded by Andrew Harris in 1892, and carried on under his leadership until 1913. The Dominion Sewer Pipe and Clay Products Industries was founded by Thos. Kennedy in 1903, began operations early in 1905, and he is still the leading spirit in its administration.

Besides the three plants in Ontario, four others are manufacturing sewer pipe in the Dominion of Canada. The Standard Clay Products Company operate a plant at New Glasgow, N. S., and one at St. Johns, Quebec. These plants evidently use a fire clay or mixture. The tile fire to a dark reddish brown and are of good quality.

Another plant is operated at Medicine Hat, Alta., firing with natural gas. Their clay is brought a distance of 300 miles from Willows and Ravens Crag, Sask. Still another plant is operated at Kilgard, B. C., where fire clay is used. Another plant was started at Carmen, Manitoba about 1913. They were endeavoring to make sewer pipe from blue shale but after experimenting about a year with mixtures without success, the war coming on in 1914, they were forced to discontinue.

Three companies produce practically all the sewer pipe used in Ontario. Some pipe is shipped to other provinces.

Clay Used in Ontario

As there is no fire clay in Ontario, all three plants use the surface clays from Waterdown. This deposit is about six miles from the Hamilton plant, thirty-two miles from Mimico and thirty-four from Swansea. The clay covers about six square miles on the Grand Trunk Railway between Toronto and Hamilton.

The clay used in Ontario is known as Medina or Queenston shale. No doubt at one time it was solid shale, the same as underlies the clay. Weathering and leaching have disintegrated the top portions of the shale. By using care in gathering, this loose material makes a good sewer pipe, very strong. It takes a good glaze of dark maroon, almost black.

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb., 1925. (Heavy Clay Products Division.)

This clay is in a rolling country with ridges 40 or 50 feet above the level with practically no clay on the top. The usable clay is confined to the valley and sides of the hills about half way up.

As a rule there is only about two feet of good clay. Often in trying to get more we run into an excess of lime, which spoils for glazing our better class of clay. The ground is very uneven and considerable underbrush has to be removed leaving many small roots which have to be eliminated by dry pans and screens.

Analysis of Our Clay The analysis of our clay is as follows: SiO_2 65.04; Al_2O_3 16.14; Fe_2O_3 6.37; CaO 0.80; MgO 21.7; Na_2O 0.64; K_2O 3.21; B_2O_3 0.12; ignition loss 5.98.

Method of Clay Gathering Each of the three companies use a different method in gathering their clay. For many years we loaded our clay with teams and scrapers, plowing at first and taking sods and roots to a convenient dumping place. The cleaner clay was loaded on dump cars of about two yards capacity, transferred to a siding and there dumped into gondolas of 30 to 35 tons capacity. For the past two years we have used a Bay City gasoline shovel with splendid success. It dips too deep sometimes, or the foreman is not careful enough in testing with acid as he goes along, and consequently we get an excess of lime sometimes with bad effects on the glaze.

The Dominion Sewer Pipe Company have for many years gathered their clay with a drag line. The Hamilton plant use a ditching machine and load directly into motor trucks transporting it to the plant without further handling.

Our raw material which should be cheap becomes a very expensive item before it ever reaches the factory. A rough estimate for freight and loading charges for our plant, using about 600 cars a year, amounts to $30,000 annually before we put a shovel in it at the factory.

Clay Drier and Storage Another difficulty in a wet season is the moisture content of the clay. Clay containing an excess of moisture will not grind or will grind only so slowly that we cannot get clay fast enough to run. To overcome this, we have two large clay sheds about 100 feet long by 35 feet wide with cement floors underlaid with steam pipes, about 12 inches apart. Through these pipes is passed part of our exhaust steam in the daytime and live steam at night. Wet clay is spread on the floor for twenty-four hours of drying.

These sheds are used as storage for winter supply. We try to have the sheds filled by the end of October. This gives us material to run from two to three months while frost is in the ground and the clay too wet to work.

Pipe Manufacturing

Clay Preparation After the clay passes the dry pan and screens it goes to storage bins to be drawn as needed. It is tempered in wet pans to suit the size of pipe being made.

Use of Grog In the larger sizes from 12 inches up we put up a certain amount of grog or broken pipe. The grog is ground in a special dry pan. The amount varies according to the size of the pipe; two shovels for 12-inch pipe and seven or eight shovels of grog to each pan of clay for 24-inch pipe. The grog keeps the clay open so that carbon and gases contained in the thick walls of the pipe may pass out in firing without blistering or splitting the ware. This has worked successfully in all the Ontario plants when enough grog has been added.

Pressing and Drying Our presses are placed on the second floor in each of the three factories. The pipe are dried on slatted floors with steam pipes underneath on the second, third and fourth stories. As the pipe are made they are elevated or lowered to the desired location, the press floor usually being reserved for the larger size of pipe. Drying requires from one week to ten days.

Kiln Firing

Our drier floor capacity is about six kilns, so we usually set from four to six kilns per week. Last year with eight kilns, we fired 240 kilns of ware.

Firing Schedule Until 1924 we usually took from six to seven days to watersmoke and fire. On my return from the Convention of this SOCIETY at Atlantic City last year, we decided to reduce the firing schedule. We fired off three or four kilns in 96 hours, or 4 days. On opening these kilns we found that while they were fairly well glazed in the larger sizes, a black cord appeared but no bloating. We came to the conclusion that the fire had not had time to soak through after watersmoking which takes about 60 hours.

Our next experiment was on a five day basis for the full firing time from lighting up. This was held throughout the year, cutting our average firing time to 115 hours. We were able to make a big reduction in fuel, time and labor, and have more use of the kilns. According to our pyrometer our kilns fired off at from 1790° to 1830°F but cones show that our heat is around 2000°F.

Our clays have a very narrow temperature vitrification range. Great care has to be taken when finishing and salt glazing. One extra fire may cause a loss of nearly all the top pipe and two may put it down into a heap.

In salt glazing one or two shovels of ground manganese ore, as fine as we can get it, are added to each barrow of salt. This gives a darker color than can be obtained with the plain salt. Out of the 240 kilns fired last year, we scarcely had one pipe that went down, but some were underdone on the bottom, due partly to flues becoming blocked.

We set our kilns two high between the bags, next courses three high, and the center of the kiln four high, the larger sizes in the center.

Cooling and Drawing of Kilns

In cold weather all fire holes are closed when through firing to avoid checking the ware. The kiln is cooling thus for three days, when it is opened and drawn. In warm weather this precaution is not taken as the ware is not so likely to check.

On drawing from the kiln the ware is sorted and loaded either on cars, trucks, or stock piles, six men carrying out, three are on one horse lorries, and three pile on the yard. The setting and drawing are both done by piece work.

Piece Rate

My own experience in the clay industry dates back to 1906 when I took over a brick plant that failed the year before. We instituted piece rate and succeeded. In 1919 when I became associated with the sewer pipe industry, I immediately began to work at a piece rate basis of manufacturing. The plant was in poor physical condition. I took charge about Christmas time. The stock of clay on hand was small and the time did not seem opportune to try out the idea. The company was paying good wages for a very low production. It seemed impossible to run one hour without a stop to adjust something or take a bolt or nut from the die, which, no doubt, had been deliberately thrown into the clay so that they might have a rest.

When I mentioned piece-work to the men it had the same effect as shaking a red flag in front of a mad bull. The owner grasped it as a possible means of salvation, for we could see no other way out of the difficulty. We drafted a price list, and spent a month on much needed repairs. In the spring with new clay shipments coming in, we set a day to put our new plan to a working test.

The men were guaranteed at least as much as they were being paid. We started on 4-inch pipe, and where formerly they would make 300 an hour they stepped up to 600 and 700 an hour. During 1924 our average run on this size of pipe has been 760 per hour. All other sizes have been in proportion. We have no regrets for making the change.

We have made two changes in our piece rate. About two years ago we made a cut of about 5% and another 5% cut has just been made operative.

We have extended our piece-work to kiln setting and drawing, unloading coal and clay. We formerly worked ten hours a day but for the last two years 44 hours is a full week's work, and many times have to slow down our presses because of shortage of room in the factory.

The setting gang would take the full ten hours to set a kiln. At the present time a gang of eight men will set a regular kiln in six hours or three in two days. Our drawing gang of twelve men who formerly took the full day to draw a kiln and load the trucks will now draw a kiln in four hours with ease, leaving the balance of the day for other yard work.

Our men are covered under the Workmen's Compensation Board when at work. We also carry an Insurance Policy of from $500.00 to $1000.00 on every man connected with the plant who has been with us over six months. This also carries sickness and accident benefits when not around the plant, and a nurse when needed. To our idea this is all good business as a contented man is an asset to any company and will do better work willingly when treated as a man.

For the past four years we have had meager labor turnover. Our conclusion is that day work is only a makeshift and that piece-work rate is practical and more satisfactory to all concerned.

Ontario Sewer Pipe and Clay Products, Ltd.
Mimico, Ontario

THEORY OF EVAPORATION WITH SPECIAL REFERENCE TO THE EFFECT OF AIR VELOCITY AND OF MOISTURE DIFFUSION[1]

By A. E. Stacey, Jr.

ABSTRACT

This paper discusses the fundamental principles of drying and shows their practical application to the problems in the drying of clay ware.

Fundamental Concepts

The initial rate of evaporation of water from a clay containing from 25% to 40% of water is practically the same as the rate of evaporation from a free liquid surface. So, for the sake of simplicity in discussing the laws of evaporation, let it be assumed that we are dealing with evaporation from a free water surface such as in a shallow pan.

Vapor Pressure Molecules are constantly in motion varying in intensity and magnitude with temperature. This movement of water molecules creates a definite pressure or force acting against the mutual attraction of the molecules, tending to cause their separation. This pressure within a body of water is known as the vapor pressure or vapor tension.

The molecules near the surface, due to their movement, will have a tendency to leave the body of the liquid and pass away in the form of vapor. An enclosure over the surface of the pan will restrain the vapor leaving the liquid and build up a pressure in the enclosure. Evaporation will proceed at a gradually diminishing rate until the pressure in the container becomes equal to the vapor pressure of the liquid. When this equilibrium is established, the number of molecules leaving the surface of the liquid will equal the number of molecules returning to the surface from the vapor. The pressure of the vapor in the vessel will then equal the vapor pressure of the liquid. Further evaporation will not take place. Under these conditions the enclosure is said to be saturated with the vapor.

The rate of evaporation varies directly with the difference in the vapor pressure of the liquid and the vapor pressure above the liquid.

These pressures are measurable directly with a manometer. At 78°F, the pressure is 1″ mercury, at 98°F 2″, etc. It is interesting to note that within certain limits the vapor pressure approximately doubles for every increase of 18°F.

Effect of Evaporation on Temperature of Liquid If no heat is added to the liquid or to the enclosure above the liquid, heat is taken from the liquid by the molecules leaving the surface, thus cooling the liquid. When the liquid cools to a

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[1] Recd. April 29, 1925.

point where the vapor pressure of the liquid in the ware equals the vapor pressure of the vapor in the enclosure, evaporation will cease.

In this case we have assumed that evaporation took place only as the result of the heat in the liquid. If above the surface of the liquid there is dry air at a temperature higher than that of the liquid the heat from the air would tend to replace the heat of evaporation lost by the liquid. Evaporation would then proceed until equilibrium is again reached.

If there is a constant supply of heat and the vapor pressure in the vessel does not accumulate, the rate of evaporation will remain constant for there will be a constant difference between the vapor pressure in the air and in the water. This is what happens in a drier without air circulation. The air of the room is heated by coils, and by conduction the air heats the moisture in the material thus maintaining the rate of evaporation.

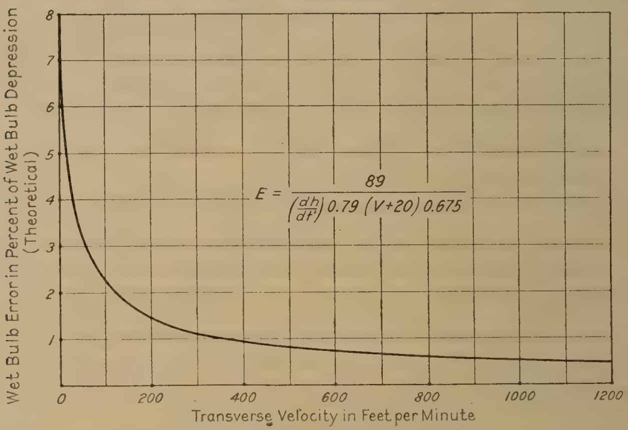

FIG. 1.—Experimental observations of wet bulb errors at 102°F (Carrier and Lindsay).

Practical Observations and Applications

Measurement of Vapor Pressures

While the vapor pressures can be measured directly, in practice it is much more convenient to make psychometric readings with a wet and dry bulb thermometer and, by a reference table, indirectly obtain the same values. The dry bulb thermometer registers the temperature above the surface of the liquid. The difference in readings of the dry and the wet bulb thermometers is an approximate measure of the heat head which causes continuous evaporation, or

$$\frac{t_1 - t'}{e' - e_0} = \text{constant}$$

t_1 = dry bulb
t' = wet bulb
$e' = P_{wb}$
$e_0 = P_{dp}$
wb = wet bulb
dp = dew point

This is a convenient means for determining the evaporation power of air in a drier. For example, other conditions being equal, a difference between the *wb* and *db* of 20° would cause evaporation to proceed at twice the rate as if the difference were 10°.

Velocity of Vapor Diffusion

Without circulation the rate of evaporation is retarded due to slow diffusion of vapor at surface of the liquid and will cease entirely as soon as a balance in heat is obtained. In case of the open pan water surface, if the supply of heat is constant and the water vapor is carried away by the air as it leaves the surface, the rate of evaporation will increase in almost direct proportion to velocity increase when the air velocities are above 300 feet per minute. With air velocities less than 300 feet per minute there will be a variation from the straight line relationship between the rate of evaporation and the velocity, due to imperfect diffusion of the vapors from the surface. This variation has been studied by Carrier and Lindsay in their work on the error of the wet bulb temperature. Their results are illustrated in Fig. 1.

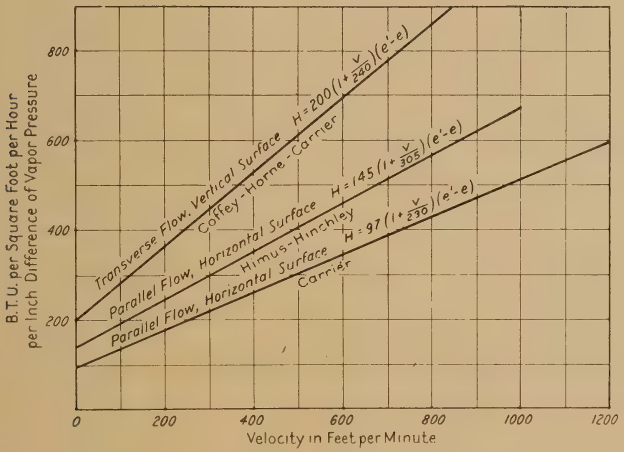

Fig. 2.—Heat transmitted by evaporation from a free water surface.

Figure 2 shows the data obtained by others both for the rate of evaporation from water surfaces parallel to the path of the air and also for vertical surfaces perpendicular to it.

The equations of these curves may be written as follows:

For the flow of air parallel to a horizontal surface—

$$H = 97\left(1 - \frac{V}{230}\right)(e' - e) \text{ (Carrier)}$$

For flow of air transverse to a vertical surface—

$$H = 200\left(1 - \frac{V}{240}\right)(e' - e) \text{ (Coffey and Horn) (Carrier)}$$

H = B.t.u. per sq. ft. per hr.
e' = vapor pressure of the water corresponding to its temperature

e = vapor pressure in the surrounding atmosphere
v = velocity of the air in ft. per min.

It is of special interest to note that the effect of impact of the air against the surface is approximately double that of air passing parallel to the surface. Furthermore, that evaporation increases approximately at a constant rate for every 230 feet increase in velocity. That is, at 230 feet per minute velocity the evaporation is twice that in still air, at 460 feet per minute velocity it is three times, etc.

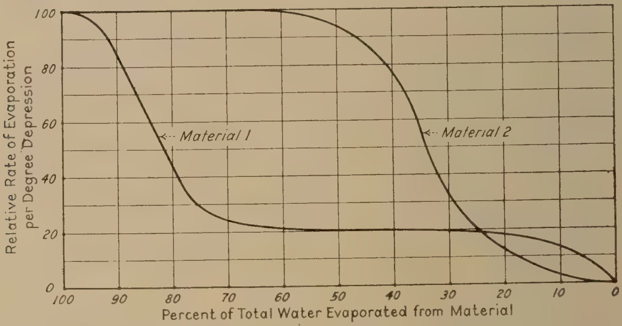

FIG. 3.—Variation of rate of evaporation with moisture content.

Diffusion In the above discussion it has been assumed that evaporation took place from a free moisture surface. However, in ceramic ware the case is more complex. In clay ware the rate of evaporation is limited by the rate of diffusion, that is, by the rate at which moisture will flow from the interior to the surface. For small wet bulb depressions, however, the rate of evaporation is approximately the same as from a free water surface.

In ceramic ware there is a maximum rate of diffusion of moisture for each temperature. An increase of velocity of air beyond that for maximum rate of diffusion at a given temperature will have no appreciable effect on the rate of drying.

The rate of diffusion of moisture in the ware will vary with the temperature. The vapor pressure of the moisture in the piece will increase with temperature.

Figure 3 illustrates the diminishing rate of evaporation per degree depression due to drying of the surface. These curves are from actual tests on ceramic ware in a commercial drier. The 100% line indicates evaporation from a free water surface and may be used as the datum line. For material No. 2 the rate of evaporation held up fairly well and for the entire run the rate equals about 66% of the theoretical. In material No. 1 the average evaporation rate was not greater than 30% of free moisture. This would indicate that surface drying was exceeding the rate of diffusion of the moisture in the ware.

Conclusions

1. The rate of evaporation varies with the wet bulb depression of the atmosphere surrounding the material to be dried.
2. The rate of evaporation from a free liquid surface increases the same amount for every 230 feet per minute increase in velocity of the air passing over the surfaces.
3. The rate of evaporation is approximately twice as great from a surface transverse to flow of air as from a surface parallel to the flow of air.
4. The rate of diffusion of moisture in the ware is a function of the temperature of the ware. This limits the available moisture at the ware surface and hence the effective air velocity at each temperature.

A NOTE ON COMPARISON OF ENGLISH VS. ORTON PYROMETRIC CONES[1]

By Sandford S. Cole[2]

ABSTRACT

The English made pyrometric cones from 10–32 inclusive were compared to Orton cones for fusion values. The results are expressed in Orton cones. The work was done in a pot furnace and the comparison was intended to give values for this type of work. A drawing shows the position of English as to that of Orton cones.

In the course of our work on refractories, The Koppers Company Laboratories have found it necessary to obtain a comparative value of the cones used in England for fusion values and these here produced by Dr. Orton. A set of cones from numbers 10 to 32 inclusive was sent from England and tested to obtain the value of the cone as expressed in Orton values.

Since the cones were to be used in pot furnace fusions the only comparison made was in a pot furnace. The cones were set, as is customary of pot furnace practice, in an alundum plaque embedded to the depth of $^1/_8$ inch. The cones were the small size about the same as the Orton cones 26 to 40. The cones were set in general in this manner: The two Orton cones next lower in value than the English, then the English and then the Orton cone of the same value and one of higher value. The plaque was removed from the furnace when the English cone touched down. The fusions were re-run and checked so as to be certain that there was no furnace misbehavior. The furnace was heated as near to the A. S. T. M. rate as was possible.

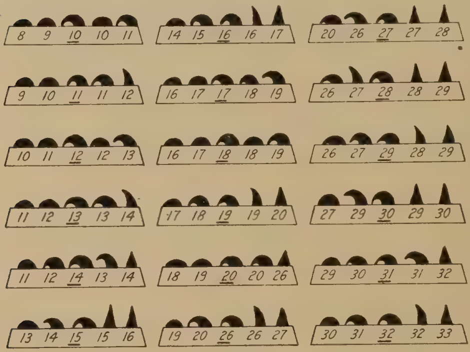

Fig. 1.[3]

In the case of some of the cones of 12–15 bloating and bubbles were found to occur. A great irregularity in the English cones was found to occur and the general conclusion reached was that the English makers of cones did not have the grade of materials used here in this country.

In Table I is given the results of the fusions. The temperature of the English cone is the one which was assigned the cones, while the tempera-

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[1] Presented at the Annual Meeting of American Ceramic Society, Columbus, Ohio, Feb. 1925.

[2] Industrial Fellow, The Koppers Company Laboratory, Mellon Institute, Pittsburgh, Pa.

[3] Plaque reading 27, 29, 30, 29, 30 should read 27, 28, 30, 29, 30.

TABLE I

COMPARISON OF ENGLISH AND ORTON PYROMETRIC CONES

English cones		Orton cones Averaging 2 or 3 runs	
Cone no.	Degrees C	Cone no.	Degrees C
10	1300	11	1350
11	1320	11	1350
12	1350	$12^1/_2$	1380
13	1380	13	1390
14	1410	$12^1/_2$	1380
15	1435	$13^1/_2$	1400
16	1460	$15^1/_2$	1440
17	1480	$18^1/_2$	1500
18	1500	19	1510
19	1520	18	1490
20	1530	20	1530
26	1580	20	1530
27	1610	$20^1/_2$	1540
28	1630	26	1550
29	1650	$26^3/_4$	1565
30	1670	$27^1/_2$	1580
31	1690	$30^1/_2$	1640
32	1710	31	1650

ture of the Orton cone is that which was accredited by the Bureau of Standards, March, 1924.

Figure 1 shows diagrammatically the position of the various cones when the English cone touched down. The center or underlined cone is the English cone. The cone number appears below each cone.

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ORIGINAL PAPERS

FORMATION OF MULLITE FROM CYANITE, ANDALUSITE, AND SILLIMANITE[1]

BY J. W. GREIG

ABSTRACT

This paper deals with a thermal and microscopic study of the decomposition of cyanite, andalusite, and sillimanite to mullite and silica, or to mullite and a siliceous liquid. The rates of alteration, the signs of the heat effects accompanying the changes, and the way in which the decompositions take place have been investigated.

The bearing on refractories is discussed.

HISTORICAL

It has long been known that both cyanite and andalusite are altered when heated to high temperatures. Saussure,[2] who first described the mineral cyanite, noted as early as 1785 that, on heating, the transparent mineral lost its color and became opaque white with a mat surface and a somewhat open texture, so that it was easily crumbled. In 1801 Haüy[3] noted that andalusite became white on heating. In 1889[4] and 1890[5] Vernadsky described experiments on cyanite. He heated the mineral in a gas furnace and found that it first lost its color, remaining transparent, and then, at a temperature of 1320–1380° measured with a Le Chatelier pyrometer, it altered quite sharply to the material described by Saussure. This took place in from 10 to 20 minutes and further heating had little effect. He states (1890) that the change takes place with liberation of heat. The product was studied in thin section and found to consist of needle crystals with positive elongation. The density was determined as 3.15–3.23 (1889). From these facts and from the fact that he was unable to affect sillimanite by heating he concluded that cyanite is changed to sillimanite and that the change is irreversible. He states (1890) that andalusite is also altered to sillimanite at the same temperature with a liberation of heat.

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[1] Recd. June 4, 1925. Presented at the Annual Meeting of the AMERICAN CERAMIC SOCIETY, Columbus, Ohio, February, 1925.

[2] Saussure, "Voyage dans les Alpes," Vol. IV, *Neuch.* (1796), pp. 84–5.

[3] Haüy, *Traité de minéralogie*, **3**, 269 (1801).

[4] W. Vernadsky, "Note sur l'influence de la haute température sur le disthuène," *Bull. soc. franc. Min.*, **12**, 447–56 (1889).

[5] W. Vernadsky, "Sur la reproduction de la sillimanite," *Bull. soc. franc. Min.*, **13**, 257 (1890).

In 1902 Beekman[1] repeated Vernadsky's experiments on heating these minerals. He determined the density before and after heating and his results agree well with Vernadsky's. Going farther, he measured the refractive index γ of the supposed sillimanite formed from cyanite, and found this to be 1.62, much too low for sillimanite. From this he concluded that cyanite does not form sillimanite on heating.

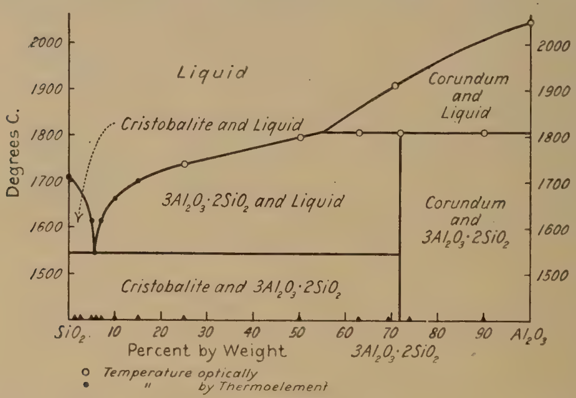

FIG. 1.—Equilibrium diagram of the system alumina-silica. Bowen and Greig (*op. cit.*).

In 1909, Shepherd, Rankin, and Wright[2] heated both cyanite and andalusite for various lengths of time at different temperatures. They concluded that andalusite at high temperatures changes to sillimanite, but very slowly. Cyanite they found to change more rapidly than andalusite. They were unable to identify the product as sillimanite under the microscope but concluded, on the basis of Vernadsky's density determination, that it was probably sillimanite. They were unable to detect any heat effect accompanying the change.

It has recently been shown by Bowen and Greig[3] that sillimanite itself is unstable at high temperatures and that the only compound of alumina and silica which is stable above 1050°C is the compound $3Al_2O_3.2SiO_2$ which has been named mullite.[1] (Fig. 1.)

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[1] E. H. M. Beekman, "Over't gedrag van distheen en sillimaniet op hooge temperaturen," *Verslagen Wisen Natuurk. Afd., Kon. Akademie van Wetenschappen Amsterdam*, **11,** 295–7 (1902).

[2] E. S. Shepherd, G. A. Rankin, and F. E. Wright, "The Binary Systems of Alumina with Silica, Lime and Magnesia," *Am. J. Sci.*, **28** [4], 293–333 (1909).

[3] N. L. Bowen and J. W. Greig, "The System Al_2O_3–SiO_2," *Jour. Amer. Ceram. Soc.*, **7** [4], 238–54 (1924).

Shortly after this Peck[2] published a paper in which he described, very briefly, the use of andalusite in the manufacture of porcelain, and the changes produced in andalusite and cyanite during firing. The result is described as an aggregate of needles of mullite with glass between. The needles are parallel in the case of andalusite and interlocking in the case of cyanite. The alteration of andalusite is said to take place sharply, at a definite temperature, and to be accompanied by a decrease of volume.

EXPERIMENTAL WORK

The three minerals cyanite, andalusite and sillimanite have the composition $Al_2O_3.SiO_2$. They differ, however, in physical properties, and in mode of occurrence. Mullite has the composition $3Al_2O_3.2SiO_2$: in physical properties it resembles sillimanite, and, to a lesser extent, andalusite. Since mullite is the only compound of alumina and silica stable at high temperatures, its formation is to be expected when any other compound of these oxides is heated to a high enough temperature. The work to be described here is a thermal and microscopic study of the decomposition of the compound $Al_2O_3.SiO_2$.

All three minerals cyanite, andalusite and sillimanite were investigated in two ways: *First*, charges of the powdered mineral were heated in a platinum-wound electric furnace, at a constant temperature, for a definite length of time, and the charge, after removal from the furnace, examined with the petrographic microscope. The temperatures were measured with a Pt:Pt 10% Rh thermocouple and a White potentiometer. *Second*. Heating curves were made using a differential thermocouple in series with a high sensitivity galvanometer.

Investigation by Heating at Constant Temperature

Cyanite The cyanite used was the beautifully transparent, slightly bluish material which occurs in a paragonite schist at Pizzo Forno near St. Gotthard. The crystals were carefully selected to be free from all foreign matter and, after crushing, the powder was examined under the microscope to be sure of its purity.

Cyanite has two perfect cleavages: the best is parallel to *a* (see sketch Fig. 2), the other parallel to *b*. There is also a parting parallel to *c*. On grinding, the mineral breaks up into plates and lath-shaped flakes with surfaces determined by these planes. When the powder is mounted for examination under the microscope, either before or after the heating, the majority of the grains lie on the *a* plane, others on the *b*. The results obtained by heating cyanite at constant temperature are summarized in Table I.

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[1] N. L. Bowen, J. W. Greig and E. G. Zies, "Mullite, a Silicate of Alumina," *Jour. Wash. Acad. Sci.*, **14**, 183–91 (1924).

[2] A. B. Peck, "Note on Andalusite from California: a New Use and Some Thermal Properties," *Am. Mineralogist*, **9**, 123–9 (1924).

TABLE I

DECOMPOSITION OF CYANITE BY HEATING

Run	Temp., °C	Time, hrs.	Results determined by microscopic examination
1	1000	48	Unaffected
2	1100	48	Exceedingly slight decomposition to mullite + silica on some parts of the surfaces of the grains
3	1160	2	Decomposition less than in 2
4	1240	1	Decomposition greater than in 2
5	1335	1	Mullite crystals 0.002 mm. (approx.) in length
6	1360	1/4	Mullite crystals 0.01 mm. (approx.) in length
7	1360	1/2	Mullite crystals 0.02 mm. (approx.) in length
8	1360	3/4	Mullite crystals 0.035 mm. (aapprox.) in length
9	1410	1/4	Crystal of cyanite 4×4×10 mm. completely decomposed to mullite + silica

Examination of the material from run 4 (1 hr. at 1240°C), in a liquid whose index matched one of the principal indices of the cyanite, showed that it was quite unaffected by the heating except that on the surfaces of the grains were minute areas the index of refraction of which had been lowered. The amount of these areas varied in different grains from approximately 0.1 % to 5% of the surface.

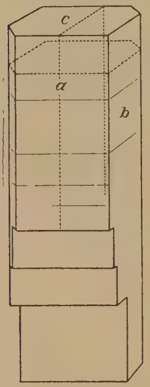

FIG. 2.—Sketch of a crystal of cyanite. The dotted lines show the orientation of sections shown in Figs. 8 and 9.

Examination of the material from run 5 (1 hr. at 1335°C) showed that practically all the surfaces, except those parallel to the *a* face were altered to the new material and that the alteration had advanced into the grain, forming a fringe estimated as 0.002 mm. wide. The surfaces parallel to the *a* face are not so much altered as the others. The interior of the grains is quite unaffected cyanite, as can be seen by grinding the powder so as to expose fresh surfaces to the immersion liquid.

When the alteration has progressed farther, as in runs 6–9, it can be seen that the new material shows exceedingly minute needles arranged parallel to each other in tiny bundles. The bundles are themselves not far from parallel (Fig. 5) and are nearly perpendicular to the surfaces from which they commenced to grow, whether these surfaces are parallel to the cleavage planes or not. The individual needles are too small in diameter to be resolved by the microscope but give the material a fibrous appearance. (See Fig. 4.) Needle crystals, then, are one of the products of the alteration: they commence at the surfaces and advance into the unaltered cyanite. The rate of growth or advance of these needles depends on the orientation: the needles that lie in the plane of the best cleavage, that is, the *a* plane, advance several times as rapidly as do those perpendicular to it.

The rates of growth of these needles, and of decomposition of the cyanite increase rapidly with temperature as shown in Table I. The length of mullite crystals given in the table is the average width of the zone of altered material measured on grains lying on the *a* plane. (See Fig. 4.)

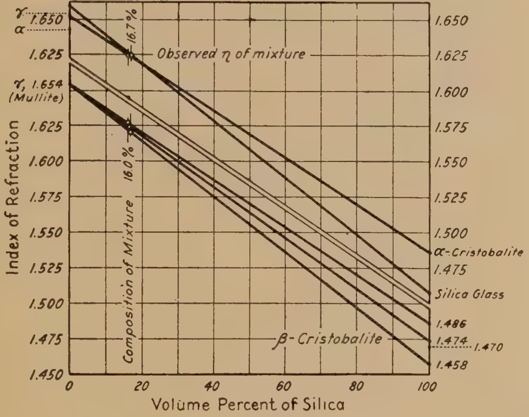

FIG. 3.—Upper part of diagram.

The index of refraction of silica glass and of α-cristobalite are joined to the observed value of the index of the product of decomposition of cyanite. At the composition of mullite the prolongations of these joins agree well with the index γ (1.654) of that compound.

Lower part of diagram.

The index of refraction γ of mullite is joined to the indices of refraction of different forms of silica. The intersections of these joins with the volume percentages of silica in the mixture give the index of refraction that such a mixture would have. These are to be compared with the observed index 1.625 ± 0.002.

It is believed that the product of the alteration is an intimate mixture of mullite, $3Al_2O_3.2SiO_2$, and silica, for the following reasons. It is known from the work of Bowen and Greig[1] that mullite is the only compound of alumina and silica stable at these temperatures. The index of refraction of this alteration product was measured by the method of immersion on material from run 8: it is 1.625 ±.002 for sodium light with "vibration plane" parallel to the elongation of the needles. Beekman[2] obtained 1.62 for this index on his material. Referring to the upper part of Fig. 3, it will be seen that the observation agrees well with this interpretation whatever the form of the silica. The sign of elongation of the needles also agrees, being positive. A charge of cyanite was held for 22 hours at 1520°C: due to this long heating at a high temperature the silica was collected into minute pellets. (See Fig. 7.) The index of refraction of the other phase could now be measured fairly closely

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[1] *Op. cit.*

[2] *Op. cit.*

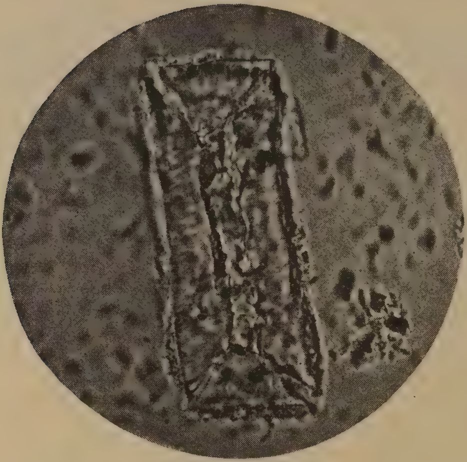

FIG. 4.—Cyanite heated 30 minutes at 1360°C × 500. The grain is lying on the *a* plane. The line of demarcation between the altered material and the unaltered central portion is clearly shown. The individual needles of mullite are not distinguishable but the fibrous structure can be made out. The clefts due to differential expansion can be seen running in from the corners.

and was found to agree with that of mullite. Dr. Wyckoff of this Laboratory has very kindly made X-ray photographs, by the powder method, of finely ground cyanite which had been heated to 1400° for 30 minutes. The pattern obtained was identical with that from mullite.

The change from cyanite to mullite and silica involves a very considerable expansion. This increase in volume causes a cleft to form at the edges of the grains of powder between the *b* and *c* cleavage faces: the clefts advance inward with the development of the mullite. They are frequently joined by a split down the center of the grain when decomposition is complete. (Figs. 4, 5, 6.) This indicates that the expansion is greatest in the direction of elongation of the mullite needles.

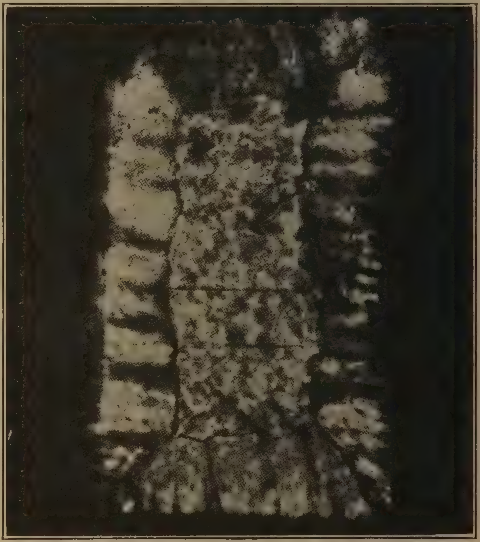

FIG. 5.—Cyanite heated 45 minutes at 1360°C, crossed nicols, × 300. This photograph brings out the orientation of the grains in bundles which are almost parallel to each other and perpendicular to the surfaces from which they grow

Crystals of cyanite were found to act as described by Saussure[1] on heating. A transparent crystal of bluish cyanite was heated with the powder in run 6 (1/4 hr. at 1360°C). After heating the color had largely disappeared. The crystal was otherwise megascopically unchanged. Examination under the microscope showed that it had behaved exactly as the powder: the index of refraction of the cyanite had not changed but mullite had developed perpendicular to surfaces and cleavage cracks.

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[1] *Op. cit.*

The crystal from run 9 ($^1/_4$ hr. at 1400°) was white and opaque: it was easily crumbled between the fingers.

The observation made here, that cyanite remains unaltered, save for the loss of color, at whatever temperature it is heated, until it decomposes to mullite and silica as described above, is in entire agreement with the observations of Shepherd, Rankin, and Wright,[1] who found it unchanged after being heated for 2 days at 1000°C. It does not agree with those of Beekman,[2] who shows a progressive decrease of index of refraction after heating, for which I am unable to account. His conclusion, however, that cyanite does not form sillimanite on heating is borne out by this work.

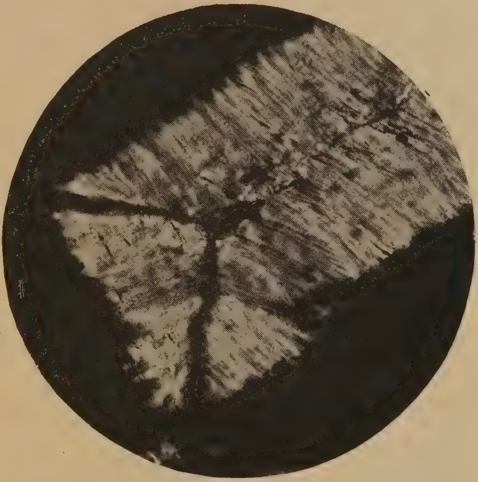

FIG. 6.—Cyanite, decomposed at 1400°C, crossed nicols, × 300. The clefts due to differential expansion are shown: the split down the center shows in places.

When cyanite is heated to temperatures above 1545°, the temperature of the eutectic between cristobalite and mullite (see Fig. 1), there is not the same regularity of structure as observed in charges heated below that temperature. There is some liquid present at the high temperatures and the crystals of mullite grow much larger. (See Figs. 8 and 9.)

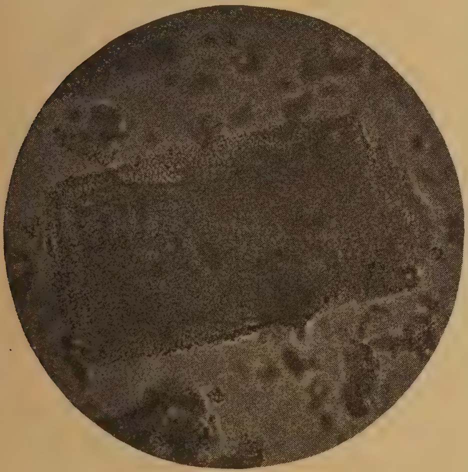

FIG. 7.—Cyanite heated 22 hrs. at 1520°C × 600. The small dots are cristobalite. Compare with Fig. 4.

Andalusite Transparent crystals from

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[1] *Op. cit.*

[2] *Op. cit.*

Minas Geraes, Brazil, were used. These crystals have a brownish color and are free from inclusions. The powder was examined under the microscope before being used and found to be quite free from foreign matter.

The results of the runs at constant temperature are summarized in Table II.

Examination of the material from run 1 (1 hr. at 1325°C) in a liquid whose index matched one of the principal indices of andalusite showed less than 1% of the grains to be affected at all. These few had minute dots of a material of low index of refraction developed on some of the surfaces. The amount is exceedingly small.

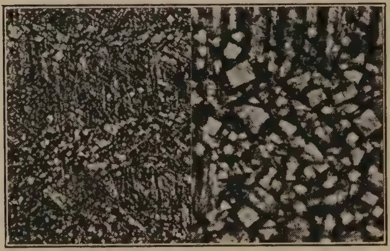

FIG. 8*a*.—Cyanite heated 1/2 hr. at 1760° C × 100. The section is cut parallel to the *c* face. Note the layers of parallel mullite needles.

FIG. 8*b*.—Same as 8*a*, × 600.

TABLE II

DECOMPOSITION OF ANDALUSITE BY HEATING

Run	Temp., °C	Time, hrs.	Results determined by microscopic examination
1	1325	1	Practically unaffected
2	1410	1	Some decomposition to mullite + silica
3	1500	2 3/4	Decomposition is greater than in 5 and less than in 6
4	1530	1/3	Mullite needles 0.005 mm. in length
5	1530	1	Mullite needles 0.01 mm. in length
6	1530	1 1/2	Mullite needles 0.02 mm. in length

In the material from run 2 (1 hr. at 1410°C) all the grains are affected. The alteration is confined to surfaces more or less perpendicular to the c' axis of the original andalusite. On parts of the edges of some of the grains the isotropic zone described below can just be made out by using the sensitive tint plate. The rest of the grain is perfectly homogeneous, unchanged andalusite.

In the material from runs 3–6 it can be seen that, when completely decomposed, the grains consist of mullite with minute dots and filaments of some material of low index which is believed to be silica. The mullite can be readily determined by measur-

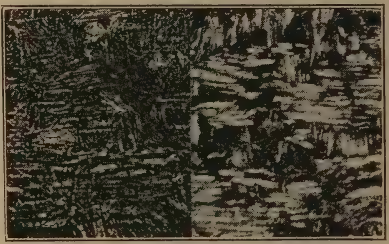

FIG. 9*a*.—Cyanite heated 1/2 hr. at 1760°C × 100. The section is cut parallel to the *b* face.

FIG. 9*b*.—Same as 9*a*, crossed nicols, × 100.

ing the index of refraction by the method of immersion. This is most easily done on small grains as the silica makes the larger ones somewhat opaque.

The mullite commences to develop at the surfaces of the grains and grows inward. The newly developed mullite is always oriented with the $\acute{c}$ axis parallel to that of the original andalusite. Since the sign of elongation of mullite is positive and that of andalusite is negative, there is a zone in which the "path difference" due to the advancing mullite is equal and opposite to that due to the remaining andalusite. This causes a dark band when the grain is examined between crossed nicols. (See Fig. 10.)

The grains formed by grinding andalusite are not, as in the case of cyanite, bounded by definite planes: they lie, under the microscope, with all orientations. Consequently it is difficult to form an idea of the length of mullite needles developed in any preparation. It is not certain, therefore, that all the grains of andalusite decompose at the same rate. The lengths given in the table are to be considered as an estimate and are more likely too low than too high.

Table II brings out the fact that, just as in the case of cyanite, andalusite decomposes to mullite and silica over a considerable range of temperature and that the rate increases rapidly with increase of temperature. Thus these alterations cannot be said to be sharp or to take place at a definite temperature.

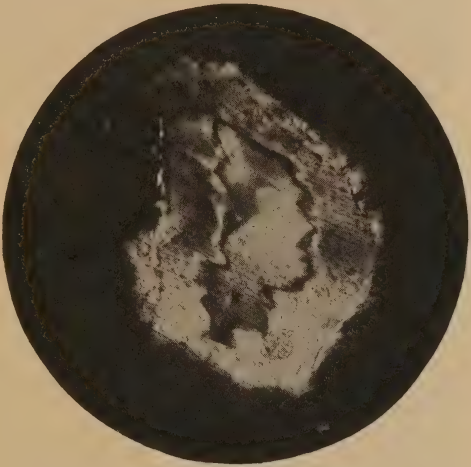

FIG. 10.—Grain of andalusite partly decomposed, crossed nicols, × 250. The uniform orientation of the mullite can be seen by the parallel lines due to the silica between the needles. The dark band shows where the "path difference" due to the mullite cancels that due to the remaining andalusite.

When heated to temperatures above that of the eutectic between cristobalite and mullite there is liquid present, and the mullite needles grow much larger, the structure remaining the same. (See Figs. 11 and 12.)

The alteration of andalusite to mullite and silica, or mullite and glass, causes the crystals to become opaque and white like porcelain, as noted by Haüy[1] and many mineralogists since. This is due to the fact that it is then composed of two substances of widely different indices of refraction intimately mixed together. As noted by Peck,[1] the alteration of andalusite does not cause the crystal to break up mechanically or become friable as in the case of cyanite.

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[1] *Loc. cit.*

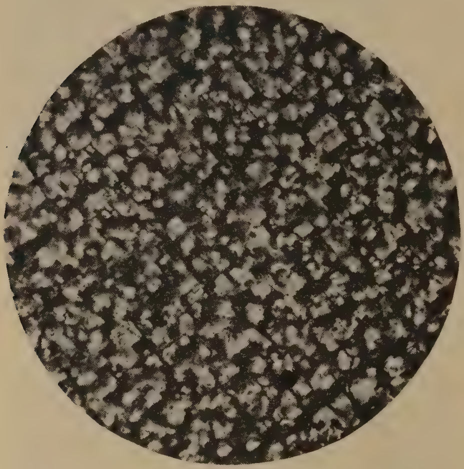

Fig. 11.—Andalusite crystal after heating at 1750°C × 500. The section is cut perpendicular to the ć axis. The mullite crystals are shown with square cross-sections parallel to each other. The dark interstitial areas are glass.

Sillimanite

The material used was the very pure fibrous sillimanite from Delaware County, Pennsylvania. It was carefully selected, and when examined with the microscope before use was found free from foreign matter.

It has already been shown[2] that sillimanite remains unchanged when heated for long periods of time at temperatures below 1545°; but that it decomposes above this temperature, yielding mullite and liquid, and that the newly developed mullite is oriented parallel to the original sillimanite.

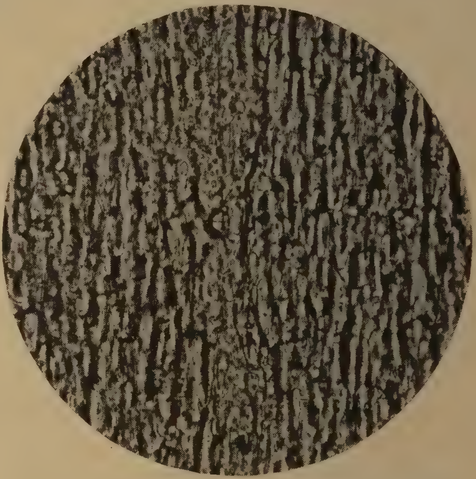

Fig. 12.—Andalusite crystal heated to 1750°C × 600. The section is cut parallel to the ć axis of the original andalusite and of the developed mullite. The dark areas are glass.

The results in Table III show that here again the rate of decomposition increases with temperature.

Unlike the other two cases, decomposition does not appear to commence at the surface of the grains of sillimanite: it appears to take place throughout the grain. A charge of powdered sillimanite raised to a temperature of 1685°C at a rate of 9°C per minute, and immediately removed from the furnace, was examined and compared with the original sillimanite. Scattered sparsely throughout the grains were

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[1] *Op. cit.*

[2] Bowen and Greig, *Op. cit.*

TABLE III

DECOMPOSITION OF SILLIMANITE BY HEATING

Run	Temp., °C	Time, hrs.	Results determined by microscopic examination
1	1345	150	Unaffected
2	1550	11	A small amount is decomposed to mullite + glass, but crystals of mullite are too small to be resolved by microscope
3	1625	3	Definitely decomposed—mullite + glass
4	1665	1	Decomposed, individual crystals of mullite readily distinguishable
5	1750	$3^1/_2$	Decomposed, mullite crystals average about 0.003 mm. in diameter

minute pellets of glass. The mass of the material was, however, homogeneous and the index of refraction was slightly lower than that of sillimanite but much higher than that of mullite. Were it completely changed to mullite and glass the index would be lower than that of mullite. It can be accounted for as an intimate mixture of unaltered sillimanite and the products of decomposition. As heating is continued the typical structure is developed: needles of mullite arranged with their $\acute{c}$ axes parallel to each other and to that of the original sillimanite with liquid between. (See Figs. 13 and 14.)

Megascopically, sillimanite changes on decomposition to a white, porcelain-like material. As with andalusite, there is no mechanical disintegration accompanying the change even when the mineral is in large pieces.

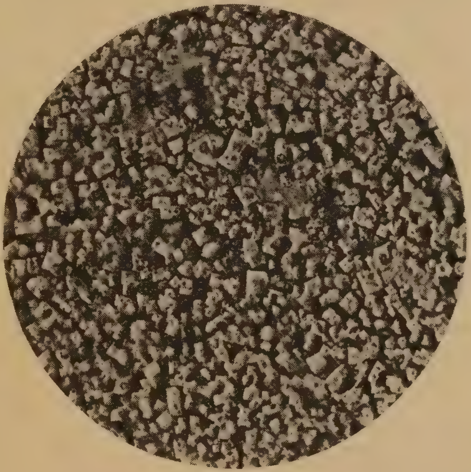

FIG. 13.—Sillimanite heated to 1750°C × 500. The section is cut parallel to the base. The square cross-section of the mullite crystals is shown. The original sillimanite was not a single crystal, but the variety known as fibrolite; hence the mullite crystals are oriented with only their $\acute{c}$ axes parallel.

Thermal Effects Accompanying the Alteration

Method of Investigation This method of investigation consists in making heating curves by means of a differential thermocouple. A charge of the material under investigation is placed in one half of a divided crucible, and in the other a charge of some reference material known to exhibit no thermal effects in the region

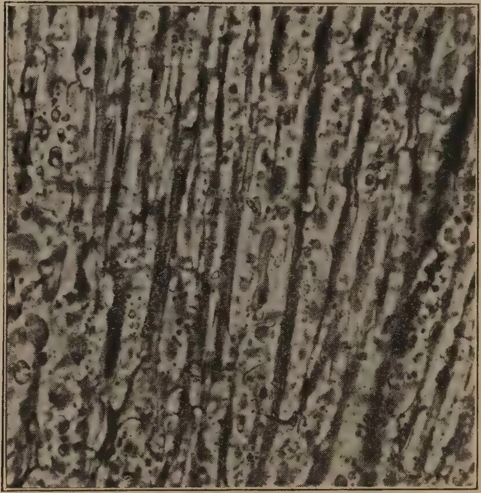

FIG. 14.—Sillimanite heated to 1750° C × 600. The section is cut parallel to the ĉ axes of the original sillimanite and of the developed mullite. Before firing the sillimanite of this photograph and of Fig. 13 was perfectly homogeneous. It is now composed of two things, mullite crystals, showing light in the photograph, and glass, which is dark. These photographs demonstrate in a very convincing way that sillimanite and mullite are different compounds.

under investigation. Readings are taken alternately on the temperature and difference of temperature at regular and frequent intervals, while the temperature of the charges is raised. The apparatus used is shown diagrammatically in Fig. 15. The thermocouple used was Pt:Pt 10% Rh, arranged as shown. When the switch S_1 is down, the temperature of the charge may be read on the potentiometer; when up, the electromotive force due to the difference of temperature of the two charges causes a current to flow through the high sensitivity galvanometer G_2. The difference of temperature is read in terms of the deflection of this galvanometer. In order to keep this deflection always at a conveniently small amount, an electromotive force opposed to that of the differential element may be introduced in the circuit. The resistances R_2 and R_3 are adjusted so that a change of setting of 1 on the resistance R_1 causes a convenient deflection of the galvanometer G_2; in this case equivalent to 5 cms. on the scale. As used the scale could be easily read to $^1/_2$ division: one division corresponded to about 0.014°C. The charges, with the thermocouples

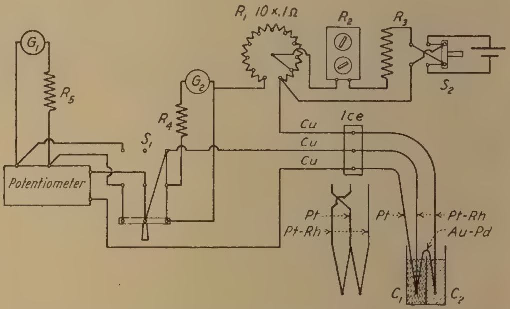

FIG. 15.—Diagram of apparatus used in differential heat runs. S_1, switch opening and closing temperature and differential circuits. S_2, switch to reverse direction of e. m. f. introduced in the differential circuit. R_3, resistance of 20,000 ohms. R_2, resistance of 9900 ohms variable in steps of 100 ohms. R_4 and R_5, damping resistances of galvanometers G_2 and G_1, respectively. C_1, charge of material under investigation. C_2, charge of reference material.

carefully centered in them, were heated in a platinum or platinumrhodium-wound electric furnace. The heating rate was not kept constant, but the resistance in series with the furnace was decreased at a constant rate: in most of the runs 0.01 or 0.02 ohm every fifteen seconds. Readings were made every fifteen seconds alternately on temperature and difference of temperature.

In each case the reference material was corundum made by firing pure precipitated alumina at a temperature in the neighborhood of 1600°C.

Cyanite A number of runs were made on the same cyanite as used for the work at constant temperature. In each case it was found that decomposition was accompanied by a marked absorption of heat, and that there were no other thermal effects. No effect is obtained on a second heating.

A typical curve is shown in Fig. 16.

As would be expected from the data of Table I, the exact position of the maximum on the curve depends on the size of grain and rate of heating. The temperatures of this maximum in different runs were 1395°, 1399°, 1399°, 1402°, 1422°. The highest temperature was obtained with a heating rate of 10° per minute.

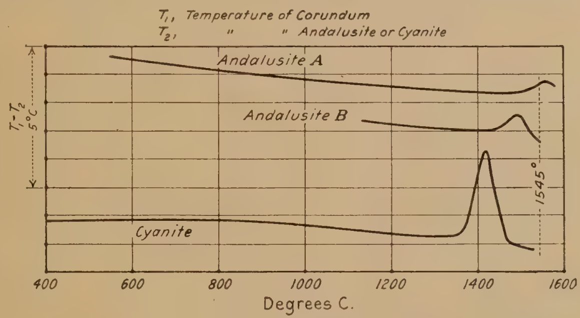

FIG. 16.—Plot of runs made with differential thermocouple, showing the heat absorption accompanying decomposition.

While this work was in progress Houldsworth and Cobb[1] published a differential heating curve made on cyanite from 0° to 1200°C. This shows an absorption of heat between 775°C and 850°C. The change to which this is due is irreversible. On the basis of the results of the study at constant temperature it is difficult to see how such a change could be possible in cyanite. An irreversible change would almost certainly leave some mark on the cyanite but the microscope reveals none. Moreover, no sign of any such effect was found with the differential element. There is no record of any microscopic examination of the material they used, and, as this mineral is particularly liable to contain foreign matter, it is thought probable that the effect observed was due, not to the cyanite, but to something else contained in it.

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[1] H. S. Houldsworth and J. W. Cobb, *Trans.* [English] *Ceram. Soc.*, **22,** 111–37 (1923).

Andalusite The material used was the same as in the work at constant temperature. As was shown by that work, andalusite alters much more slowly than cyanite and at a higher temperature. A number of runs were made on andalusite which showed only a very slight change of slope in the region of the eutectic between cristobalite and mullite (1545°C). Since the alteration proceeds from the surface inward, the smaller the grain, the shorter will be the time required to alter it completely. Curve A, Fig. 16, is a plot of a run on finely ground andalusite. It shows a definite heat absorption but it is above 1545°C. It was believed that this was due to the decomposition, so a charge was prepared by grinding andalusite for 36 hours with a mechanical grinder, and then floating off the finest material for use. The preparation was examined with the microscope and found free from contamination: the average grain was less than 0.001 mm. in diameter. The run made on this material is plotted as curve B, Fig. 16. This time there is a quite definite heat absorption below 1545°. Microscopic examination, after the run, showed that the material had been completely decomposed. The alteration, then, takes place with an absorption of heat.

The thermal effect observed in the case of cyanite and of andalusite is opposite to that which Vernadsky (1890) states accompanies the decomposition. He gives no experimental details except that he measured the temperature with a "Le Chatelier pyrometer." Considering the sign of the heat effect and the difficulty experienced in detecting it with the sensitive apparatus used in this investigation, I am at a loss to explain his observations.

Sillimanite Finely ground sillimanite was also run to see if any heat effect could be observed. No effect whatever was observed below 1545°C.

Form of Silica Present in the Product of the Decomposition

When cyanite and andalusite are decomposed by heating they yield mullite and silica: mullite 87.64%, silica 12.36%, calculated for the pure mineral. The question arises, then, as to what form the silica is in, whether amorphous or crystalline; and if crystalline, in which modification. On account of the fine state of subdivision of the silica and its dispersion in the mullite the form cannot be determined with the microscope.

Both tridymite and cristobalite when heated undergo inversions at low temperatures.[1] An attempt was made to decide the question by detecting the heat effect accompanying these inversions. The apparatus was that described above; but for this work a Pt 10% Rh: Au 40% Pd differential thermocouple was used. (Fig. 15.) This is about five times as sensitive as the Pt:Pt 10% Rh couple, but cannot be used at temperatures much above 1400°C. With this arrangement one division of the scale corresponded to a temperature difference of 0.003°C.

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[1] C. N. Fenner, "The Stability Relations of the Silica Minerals," *Am. J. Sci.*, **36** [4], 331–84 (1913).

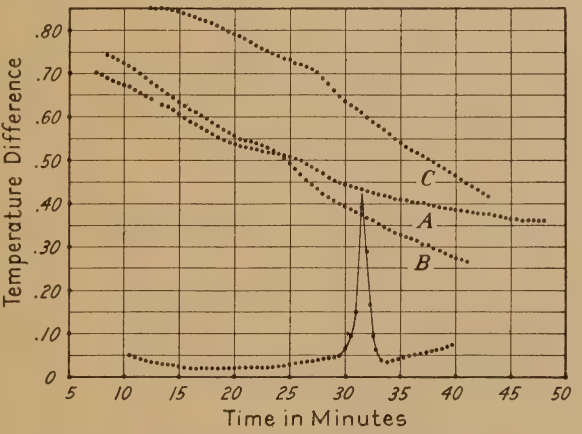
The results of this investigation are summarized in Table IV.

TABLE IV

RESULTS OF DIFFERENTIAL HEAT RUNS ON DECOMPOSED CYANITE AND ANDALUSITE

Run	Material	Microscopic examination	Result of heat run
1	"Cyanite" heated $^1/_2$ hr. at 1400°	No silica visible	No thermal effect observed
2	"Cyanite" heated $20^1/_2$ hrs. 1400–1415°	Little different from 1. Some silica has collected into grains large enough to be seen	No thermal effect observed
3	"Cyanite" heated 22 hrs. 1520° ±10°	Silica has now collected into minute pellets	Very slight effect corresponding to $\alpha \longrightarrow \beta$ cristobalite inversion
4	"Andalusite" heated 5 hrs. 1520° ±10°	Silica in minute pellets and shreds	Very slight effect corresponding to $\alpha \longrightarrow \beta$ cristobalite inversion
5	"Andalusite" heated 20 hrs. 1520° ±10°	As 4	As 4

Runs 3, 4 and 5 are plotted in Fig. 17. Although the heat effects are exceedingly small, they are real, for they are obtained each time the charge is heated. The temperatures at which the maximum heat effect was observed in different runs are given under the diagram. Considering the fast heating rate employed and the magnitude of the heat effect, the agreement is good. By comparing the break in these curves with that on



Temperatures of Maximum Heat Absorptions °C

Andalusite decomposed at 1520°± 10° 5 hours. A: 247, 249, 254

" " " " " 20 " B: 240, 240, 237

Cyanite " " " " 22 " C: 245, 243

FIG. 17.—Plot of runs made on decomposed cyanite and andalusite to detect inversion of the silica. In each case the first value was obtained for the run plotted. The lower curve is a plot of a run made on a mixture containing cristobalite 12%, corundum 88%.

the curve obtained with a mixture of 12% cristobalite and 88% corundum it will be seen that only a very small part of the silica inverts. That which does invert is cristobalite. If the rest is crystalline it must remain in the high-temperature form.

Dr. Wyckoff has kindly made X-ray powder photographs of the material used for all these runs except 5. The following are the results.

(1) No pattern except that of mullite.

(2) There is a very faint broad line which is not due to mullite. It is not definite enough to say whether it is due to cristobalite or to tridymite.

(3) A sharp, well-developed line corresponding to the most prominent line of the cristobalite pattern. It is not possible to state whether the cristobalite is in the α or β form. From the intensity of the line there is a considerable amount present; probably all the silica is there as cristobalite.

(4) Could not be certain whether or not there is any line other than those due to mullite.

TABLE V

CORRESPONDENCE OF CALCULATED WITH OBSERVED INDEX OF REFRACTION OF THE PRODUCT OF DECOMPOSITION OF CYANITE

Form of silica assumed	Density	Volume % of silica	Index of refraction	Index of refraction of mixture	
				Calculated	Observed
α-cristobalite	2.333[1]	16.0	1.486[1] (mean)	1.627	
β-cristobalite	2.277	16.4	1.474	1.625	
α-tridymite	2.270[1]	16.4	1.471[1] (mean)	1.624	
β_2 tridymite				1.624	
Silica glass	2.206[2]	16.7	1.458[3]	1.621	
Index of product of decomposition of cyanite					1.625 ±0.002

Density of mullite 3.156.

Index of refraction γ of mullite 1.654.[4]

Values for β-cristobalite calculated on basis of 2.4%[5] volume change at the α-β inversion.

The change in tridymite at the inversion is too small to affect the value of the index of refraction of the mixture in the third decimal.

There is a progressive increase in the size of the grains of silica in 1, 2 and 3. The broad nature of the line obtained in the X-ray photograph of 2 is probably due to the exceedingly small size of the crystals of silica. If these crystals were still smaller the line would not be detected.

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[1] C. N. Fenner, "The Stability Relations of the Silica Minerals," *Am. J. Sci.*, **35** [4], 331–84 (1913).

[2] Day and Shepherd, "The Lime-Silica Series of Minerals," *Am. J. Sci.*, **22** [4], 276 (1906).

[3] J. W. Gifford and W. A. Shenstone, "The Optical Properties of Vitreous Silica," *Proc. Roy. Soc.*, **73**, 201–8 (1904).

[4] Bowen and Greig, *op. cit.*

[5] P. Braesco, "Étude des points des transformation par une methode dilatometrique," *Ann. Phys.*, **14**, 5–75 (1920).

As stated above the index of refraction of the material formed when cyanite is decomposed was measured and found to be 1.625 ± .002. Since the index is an average of that of the silica and γ of the mullite, it depends on the form in which the silica is present. In Table V are given the results of a calculation of the indices that the mixture would have with the various forms of silica. This is not a very sensitive test, yet it shows that the silica can hardly be there in the amorphous form: the most probable form is β-cristobalite or one of the forms of tridymite. This is shown graphically in the lower part of Fig. 3.

From the X-ray photograph of the "cyanite" of run 3 the silica is probably all cristobalite and from the results of the heating runs made on this material it is nearly all β-cristobalite. From the data on refractive index this is also the most probable modification of the silica formed immediately on decomposition of cyanite. Although, at the temperature at which this material was formed (1360°), tridymite is the stable form,[1] it is in entire agreement with experience with silica that cristobalite should crystallize instead of tridymite under such conditions. It is believed, therefore, although the evidence is not as full as might be desired, that the silica set free when cyanite is decomposed by heating is crystalline, most probably cristobalite, and that it remains in the high-temperature form on cooling, due to the extremely small size of the crystals. When these crystals grow larger, due to long heating at high temperatures, some of them invert on cooling as in the material of run 3 (heated 22 hrs. at 1520°).

Since the thermal behavior and state of aggregation of the silica in 4 and 5 (Table IV) are very little different than in 3, it is probable that, in the case of andalusite, the silica is cristobalite, only a small amount of which inverts on cooling, the rest remaining in the β-form.

Volume Changes Accompanying the Alterations

The density of mullite, made from the pure oxides by repeatedly sintering at a temperature of about 1700°C and grinding, was found by the pycnometer method to be 3.156 at 30°C. The density of silica and of the glass formed at temperatures above 1545° is much less. The densities of cyanite, andalusite and sillimanite are, according to Dana, 3.56–3.67, 3.16–3.20, 3.23–3.24, respectively. The alteration of these minerals by heating must therefore be accompanied by an increase of volume. This is greatest in the case of cyanite and least in that of andalusite. The values obtained by Vernadsky (1889) and by Beekman[2] show this increase. Peck,[3] on the other hand, states that the alteration in the case of andalusite is accompanied by a decrease of volume, but gives no measurements.[1]

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[1] Fenner, *op. cit.*

[2] *Op. cit.*

[3] *Op. cit.*

APPLICATION TO REFRACTORIES

Since the three minerals, cyanite, andalusite and sillimanite are available as sources of material for the manufacture of alumina-silica refractories a knowledge of their behavior on heating is of value to ceramists. All three are themselves quite refractory but the fusion temperature of ware made from them can be raised by the introduction of alumina. This is well brought out in Fig. 18, which is the equilibrium diagram on which the weight percentage of mullite present at different temperatures has been marked. It is to be noted that the volume percentage of mullite present is considerably less than the weight percentage. By addition of alumina the composition of the compound mullite is approached, and, since this remains unaffected up to the temperature of its incongruent melting, the amount of liquid present at any temperature is decreased.

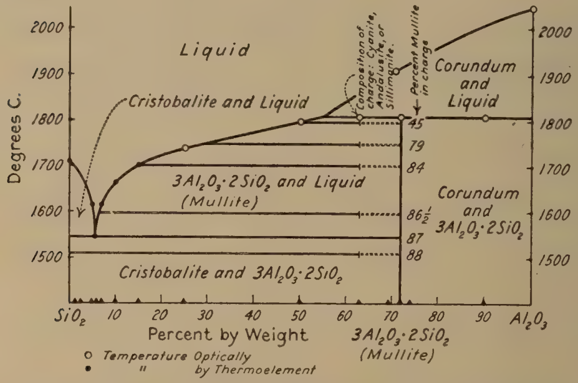

FIG. 18.—Diagram showing percentage by weight of mullite formed by heating sillimanite andalusite or cyanite.

The expansion of cyanite during the alteration to mullite and silica is so great that any ware made largely from this mineral would probably be shattered on firing. The difficulty may be overcome by changing the mineral to mullite and silica before forming it into ware. The data of Table I show that this is most readily done at temperatures above 1400°C and that then a few minutes will suffice for even quite coarse material. Since the material becomes very friable during the alteration it can be more easily ground afterward than before.

With either andalusite or sillimanite no trouble due to expansion is to be expected.

Since the silica does not invert on cooling, there is no likelihood of trouble from volume changes due to it.

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[1] While this manuscript was in press Peck published density determinations which show an increase in volume. (A. B. Peck, "Changes in the Constitution and Microstructure of Andalusite, Cyanite and Sillimanite at High Temperatures and Their Significance in Industrial Practice." *Jour. Amer. Ceram. Soc.*, **8**, 407–29 (1925).)

SUMMARY

The three minerals, cyanite, andalusite and sillimanite are decomposed, on heating, to mullite and silica, or to mullite and siliceous liquid. The silica is probably cristobalite.

The lowest temperatures at which the alterations take place are different for the three minerals: cyanite alters at the lowest temperature, sillimanite at the highest. For all three there is no definite temperature at which the mineral decomposes sharply to the new phases, and below which it remains unaffected for an indefinitely long period.

In the cases of cyanite and of andalusite the alteration commences on the surfaces of the grains and advances inward. In that of sillimanite the change seems to take place throughout the grain.

In all three minerals the rate of decomposition increases rapidly with rise of temperature.

When andalusite and sillimanite are decomposed, the newly formed mullite crystals are oriented parallel to the original crsytals: with cyanite this orientation is determined by the surfaces from which the mullite grows.

The decomposition of cyanite and of andalusite is shown to be accompanied by an absorption of heat.

In all three cases the new phases formed are of lower density than the original mineral, so there is an expansion accompanying the decomposition.

Geophysical Laboratory
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DISCUSSION

D. W. Ross: In the case of the cyanite, you speak of the crystal in the dry powder. When they are in the melt how do they develop? Does it radiate out in the melt?

J. W. Greig: Whether the cyanite, or the mullite which is developed on decomposition of the cyanite, will be attacked by the melt will depend on the composition of the melt, and on the temperature. I have not investigated the effect of a melt on the decomposition of cyanite. In the course of the work I have just outlined I have examined a thin section of cyanite over which the liquid, formed by melting a low grade fire brick, had flowed. The decomposition had taken place precisely as if there were no melt present, that is, as shown by the photographs. The liquid had penetrated the openings in the crystal, formed by cleavage cracks and fractures; into the liquid, which filled these openings and surrounded the crystal, long needles of mullite had radiated from the decomposed cyanite. In general I should expect that, at temperatures above 1300°C, the decomposition of the cyanite would proceed as in the dry powder and that whether or not there was attack on the mullite would be determined by the composition and temperature of the melt. Mullite is stable in contact with melts of silica and alumina, with smaller amounts of other oxides, through quite wide ranges of temperature and composition.

I have not investigated the rate of attack of mullite by melts in which it is not stable.

W. J. McCaughey: Does the color change?

J. W. Greig: These minerals have various colors before being heated. When they are decomposed, they are all perfectly white, and opaque-like porcelain.

W. J. McCaughey: How do you tell easily sillimanite from the mullite?

J. W. Greig: The easiest way is to know where it comes from. There has been sufficient work done to demonstrate that in all ceramic ware the needles are mullite, not sillimanite. In rocks they are usually sillimanite, but not always. To decide the question they must be removed from the matrix. This may be done by leaching in *cold* hydrofluoric acid followed by other acids to dissolve the products of the reaction. The index of refraction of the individual crystals may then be measured by the method of immersion. This will usually settle the question. It is true that mullite may contain titanium and iron and the indices of refraction may be raised by them, approaching those of sillimanite. In such cases we have found the mullite to exhibit a pink pleochroism; sillimanite rarely if ever shows this pleochroism. Another method, which is not generally available to mineralogists, but which is quite decisive, is to fire the cleaned crystals to a temperature of 1600°C or 1700°C. If the crystals are mullite they will be unaffected; if sillimanite, they will be decomposed to mullite plus glass, and an examination under the microscope will readily decide the question. A fuller discussion of these points will be found in the two papers, "The system Al_2O_3–SiO_2," by Bowen and Greig[1] for last year, and "Mullite, a Silicate of Alumina," by Bowen, Greig and Zies.[2]

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[1] *Op. cit.*

[2] *Op. cit.*

PROGRESS REPORT ON THE USE OF ANDALUSITE AS A REFRACTORY[1]

By Robert Twells, Jr.

ABSTRACT

An account is given of the development of andalusite for refractory purposes with descriptions of some uses to which it has been put.

Introduction

History The discovery of a large deposit of andalusite and the development of its use on a commercial scale makes a story which sounds like a romance. The results, however, were only attained through patient search, thoroughly scientific research and careful plant control, extending over a period of years. The use of andalusite in producing the "sillimanite" spark plug porcelain has been most successful. In fact many new and valuable results have been attained which could not have been foretold. The Champion Porcelain Company is, of course, chiefly concerned in the use of andalusite in heat-resistant vitrified porcelains. An interesting development, however, has been the use of the andalusite as a refractory. This work is still in the experimental stage and final results are not yet available.

The Andalusite The andalusite herein mentioned has been fully described by Peck[2] and the description need not be repeated. Suffice it to say that the deposit is found at an elevation of 10,000 feet on White Mountain of the Inyo range in California. Its composition is that of a rather pure andalusite with comparatively small amounts of several associated minerals of which corundum and pyrophyllite are perhaps the chief. Quartz is confined chiefly to small veins crossing the mass, and is readily sorted out. "Generally the material runs at least 75–85% andalusite upon microscopic examination. A typical chemical analysis from a sample representing a carload shipment, recalculated to an Al_2SiO_5 basis, will show over 90% Al_2SiO_5. Such an analysis follows:

Analysis	
SiO_2	33.78
Al_2O_3	56.89
H_2O	0.37
Ignition loss	3.67
Other determining constituents	5.37
	100.08

Equivalent to	
Al_2SiO_5	94.18
SiO_2	0.22
Others	5.60

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb. 1925. (White Ware Division.) A partial report of some work carried on by several persons over a period of time in the Research Department of the Champion Porcelain and Jeffery-Dewitt Insulator Companies.

[2] A. B. Peck, "Note on Andalusite from California; A New Use and Some Thermal Properties," *Am. Mineralogist*, **9**, 123 (1924). This article has been freely drawn upon for microscopic and mineralogical information.

The fact that the chemical analysis generally shows higher Al_2SiO_5 than is indicated by the microscopic examination is due to the frequent occurrence of corundum in the material."

Physical Changes on Firing

The behavior of andalusite under firing is important. "Up to its inversion point andalusite retains all of its original optical properties except for the formation of small glass-like inclusions which apparently represent the fusion of included impurities." At about cone 13 "the clear homogeneous grains of andalusite give way to grains composed of fibrous or columnar crystals, each crystal parallel to the adjacent one with a narrow strip of glass between. The result is instead of a clear grain, a grain composed of a group of parallel crystals having all of the optical properties of $3Al_2O_3.2SiO_2$, with a highly siliceous glass between each."

During inversion the andalusite does not outwardly loose its original form. In fact it is possible to exactly refit together the jagged edges of two halves of a lump of andalusite, one half just as it came from the mine, the other half after being fired to cone 18. This constancy of volume is a most important advantage of andalusite. For comparison cyanite expands greatly at its inversion point (about cone 11) and breaks down to a chalky friable mass. On the other hand some highly aluminous refractories such as diaspore and bauxite have the tendency to shrink continuously under load at high temperatures.

Change in Chemical Constitution

When the original work to utilize andalusite was started its ratio, 1 Al_2O_3 to 1 SiO_2, was thought to be ideal for refractory purposes. Bowen and Greig[1] have since shown that the ratio of $3Al_2O_3$ to $2SiO_2$ makes theoretically the better refractory for very high temperatures. This superiority is due, not so much to the relatively small difference in their fusion points as to the fact that the 1:1 ratio starts to melt at a much lower temperature due to the formation of $3Al_2O_3.2SiO_2$ crystals and a highly siliceous liquid.

As Bowen and Greig explained, for many refractory uses, the presence of a small amount of siliceous liquid may even be desirable owing to its bonding strength and low coefficient of expansion. Its high viscosity would also tend to prevent ready deformation under load. At somewhat moderate temperatures andalusite refractories can thus be expected to be fairly constant in volume, resistant to fracture by thermal changes, and stronger under load than fire clay refractories. For very high temperatures it might be desirable to mix diaspore or bauxite with the andalusite in amounts sufficient to give the entire refractory the $3Al_2O_3.2SiO_2$, or mullite ratio.

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[1] N. L. Bowen and J. W. Greig, *Jour. Amer. Ceram. Soc.*, **7** [4], 238–54 (1924).

The natural mullite itself has unfortunately not yet been discovered in a commercial deposit. Andalusite on the contrary is available in large quantities at moderate cost. The deposit is exceptionally uniform and pure, making concentration unnecessary.

Use of Andalusite as a Refractory

Load Capacity Its softening point under load, although doubtless lower than that of mullite, is still high enough to make andalusite useful for many special refractories. In a standard load test conducted at the Mellon Institute, a standard size, 100% raw andalusite brick gave a deformation of 0.38%. At the same time a sample No. 1 grade fire brick gave a deformation of 4.36%.

Fusion Point Standard cone tests of the andalusite indicate a fusion point between cones 35 and 36. It should be recalled that this deposit of andalusite is being developed primarily for its properties in a high fire porcelain. Some samples of andalusite picked especially on account of their purity gave still higher fusion tests.

Molding Property Another important property of andalusite is the ease with which it can be formed into difficult shapes. The pyrophyllite present is no doubt of considerable help in the development of plasticity and bond at this stage. Most of the andalusite refractories tried have been formed by hand tamping in steel or wooden molds. In some cases a wall or floor was rammed directly in place in a kiln or furnace. It was found practical to form a mix consisting of 100% andalusite by the use of a small amount of organic bond. Such a mixture could no doubt be readily worked in a dry press machine. Casting special refractories from andalusite was readily done with the addition of small percentages of clay. In this way several difficult shapes such as spouts and stoppers were made for glass refractories.

Bonding Experiments were made covering the use of many different bonds for the andalusite grains at high temperatures. At present, when the refractory is made by tamping, the grains are allowed to bond themselves. This they readily do when fired to about cone 18. It is thus unnecessary to use plastic bond clays which would tend to weaken the load bearing properties of the mixture.

A Service Test The refractory problem at the Champion Porcelain Company has always been very difficult. High fire porcelains are usually fired on a very short schedule. One tunnel kiln is now being operated on a 31-hour cycle. Oil is used to produce a firing temperature of cone $18^1/_4$ down. In continued use under such conditions the best flint or highly aluminous fire brick will soften and bulge under relatively small load.[1]

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[1] This approximates 10 lbs. per square inch or less at about 1450°C.

The rapid thermal changes in this plant are also very trying on the refractories. Fire clay car tops break up rapidly, their average life being from 3 to 4 months. Under these severe conditions andalusite blocks are now being used for the tops of practically all of the cars. The first of these cars has been running continuously since November 7, 1924. So far the blocks are in good condition, showing no signs of cracking or softening.

Two mixes are being tried out in this way, one coarse and one relatively fine. The mold used had the dimensions $13^7/_8''$ by $6^{15}/_{16}'' \times 2^1/_2''$. The fired blocks made of the fine mix were exactly the same size as the mold; those of the coarse mix were $14'' \times 7'' \times 2^1/_2''$. The absorption of the fine mix was 7.8%, that of the coarse mix 6.5%. A very fine mix is somewhat difficult to mold due to its springy nature; cracks form in molding which tend to open in firing. A coarse mix tends to expand slightly in its initial fire. A properly proportioned mix is not subject to these defects.

Andalusite Saggers As a sagger at this plant andalusite has not yet proved satisfactory due to the failure of the bottoms when filled with ware. The same may also be said regarding fused alumina, fused or calcined artificial sillimanite or mullite, spinel, zircon and such "super-refractories" with the exception of silicon carbide.

The reasons for these failures are the design of the saggers and the severe conditions under which they are used. The saggers themselves have a $^5/_8$-inch thickness of wall and bottom and an inside diameter of $13^1/_2$ inches. Over this span they must carry a load of about 8 pounds at a temperature of cone $18^1/_4$ down. Some saggers were made having sides of andalusite and bottoms of silicon carbide; these proved to be very good.

The andalusite at cone $18^1/_4$ down seems to have good strength in compression but is somewhat weak in tension or shear. A large number of mixes were made up to try to overcome this defect. These were tamped into $9^1/_4 \times 2^5/_8 \times {}^3/_4$-inch bars which after an initial fire were given sag tests across an 8-inch span. The cone was noted at which sagging commenced.

The best results (cone $19^1/_2$) in this test were obtained with mixes containing from 50% to 75% of calcined andalusite, the balance fine raw andalusite. In mixes containing all raw andalusite the fine grained bars stood the sag test better than the coarse grained. Clay and similar binders did not prove advantageous.

The temperature used during the initial fire of the bar proved to be important. The higher the first fire the better were the results.

None of the "super-refractories" already named, except silicon carbide, stood this test successfully at cone $18^1/_4$ down. In fairness, however, it should be stated that no attempt was made to use these "super-refractories" for saggers except under the severe conditions already mentioned. At lower temperatures, with saggers of different design we understand that some have been quite successful.

The best andalusite mixes developed would doubtless also stand up successfully in ordinary practice at cones 8 to 12 and might prove considerably better than the ordinary fire clay-grog sagger. A large whiteware manufacturer is now testing out the andalusite in this respect.

Andalusite in Standard Brick

A considerable number of standard size brick were made from a 100% andalusite mix similar to that tested at the Mellon Institute. One installation is in an oil fired test kiln frequently used for firing ware at cone 32. The andalusite brick form the side walls; high grade silicon carbide brick form an arch over the fire box and a double baffle wall at one end of the kiln chamber. The silicon carbide brick are now badly blistered. The baffle wall has twisted and partly fallen over. This would indicate that there had been an intense local heat at that part much higher than cone 32. The andalusite brick are now dark brown in color. There are some shrinkage cracks at intervals in the joints, otherwise the walls appear sound. The cracking may have been due partly to the fire clay mortar which was used.

With andalusite refractories we are now using a mortar made of 100% finely ground andalusite. This mortar works well and gives a thin joint. Other andalusite brick have been placed in installations which cannot yet be examined; for instance, in the fire boxes of a tunnel kiln and of boilers.

Andalusite as a Plastic Refractory

Another installation of andalusite was a rammed-up lining in a rotary brass smelting furnace. Previously several different kinds of refractories, including high temperature cements had been tried with poor results. The andalusite proved more successful than the others, and gave good satisfaction.

Conclusions to Date on the Value of Andalusite as a Refractory

Silicon carbide stands in a class by itself in resisting shearing loads at high temperatures; andalusite, however, seems to compare equally favorably in this respect to the remaining "super-refractories." The most valuable properties of andalusite are its constancy of volume, its good strength under compressive loads at moderately high temperatures, its resistance to sudden heating and cooling, and the ease with which it can be shaped and bonded. It is to be expected that the chief uses of andalusite as a refractory will be in places where lack of volume changes and resistance to thermal shocks are the most important requisites.

CHAMPION PORCELAIN CO.
DETROIT, MICH.

Discussion

F. H. RIDDLE: The andalusite[1] used is from the Inyo Mountains in California.

J. W. GREIG: I have seen some of this material: it has suffered considerable alteration, not on the surfaces only, but throughout the crystals, particularly to pyrophyllite, and I was wondering if this alteration caused it to be more easily formed than pure andalusite. Pure andalusite when powdered will not be plastic.

F. H. RIDDLE: Mr. Twells stated the pyrophyllite was a tremendous help in developing a little plasticity.

E. SCHRAMM: Is this material generally available, or is it going to be?

F. H. RIDDLE: Not yet, but there is a deposit there that will eventually be big enough so that it probably could be. So far, it has been used just for experimental purposes in different lines.

K. M. SMITH: Of what use can andalusite be made in whiteware such as sanitary ware? Would it be of advantage to use it in the prevention of dunting or spalling or would its color alone throw it out?

F. H. RIDDLE: The color of this particular deposit would throw it out. It fires to quite a dark tan color. However, there are parts of the deposit which are practically pure white and the treating of this particular deposit would possibly make it of use.

K. M. SMITH: Would additions of this pure andalusite be of benefit to the sanitary ware at the ordinary sanitary temperatures cones 9 or 10?

F. H. RIDDLE: In a comparison of the thermal expansion of quartz and of this material and of the bodies in which these materials are used there will be a noticeable difference in favor of the andalusite. Whether it will be of any benefit is something that has to be proven out. Small experiments look favorable, but large scale production has not been attempted as yet other than at high fires. Above cone 15 it is absolutely all right. However, down below that, it looks very favorable.

J. W. GREIG: What percentage of pyrophyllite was found in this material?

A. B. PECK: There is an average of about 5%. It varies a good deal. There are little pockets where there is a great deal; then there is a lot of material that is practically pure and uncontaminated.

J. W. GREIG: What is the difference, after it has been raised to a high temperature, between this material and fresh andalusite from other sources?

A. B. PECK: Microscopically there is no difference between the two; apparently though, it works better.

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[1] A. B. Peck, "Note on Andalusite from California: a New Use and Some Thermal Properties," *Am. Mineralogist,* **9**, 123–9 (1924).

J. W. Greig: Is it better than cyanite or sillimanite?

F. H. Riddle: From our experience it is very much better, but we have naturally shown more interest and have gone after our particular material a great deal more intensively than we have things which were not available commercially.

J. W. Greig: These refractories really are not andalusite after they have been fired, but are mullite plus siliceous glass or silica. One made from cyanite or sillimanite would be the same in this respect.

F. H. Riddle: The ease with which they change to the mullite and excess silica and the temperatures at which they make that change also have a marked effect on the quality of the product. There is a noticeable difference.

We have made synthetic mullite. The mullite crystals are very sharp, fine grain crystals and very much more difficult to work than is this material.

J. W. Greig: This andalusite would be much easier to work into ware because of the impurity which is in it than would pure mullite.

F. H. Riddle: It so happens that this andalusite has some fluxes in it, and these fluxes are the fluxes which are beneficial to a porcelain in which you wish a high hot dielectric resistance at higher temperatures. There are no alkalis whatever present, at least only traces, and of course, in this particular case it is a great advantage, but for refractories, as Mr. Twells stated, a different type of andalusite from the other parts of the deposit would be preferable or else this one purified.

J. B. Davis: Does andalusite have any effect on platinum? Would it make platinum wire brittle or cause it to crystallize?

J. W. Greig: Andalusite, free from iron, will have no effect on platinum. We have used tubes of this composition on which to wind the platinum of our electric furnaces, and there has been no action on the platinum. These tubes were not made from andalusite, but are of practically the same chemical composition.

F. H. Riddle: We have made up tubes of 1:1 mixtures vitrified at cone 32 and have had very good success with them. It is really very refractory and yet gas-tight and so prevents impurities from getting through the tubes and attacking the platinum.

J. W. Greig: Marquardt porcelain, the material to which I refer, is of practically the same composition. Some grades contain more alumina, approaching the composition of mullite, while others are nearer the 1:1 ratio of sillimanite. They contain very little in the way of impurities. This material, when fired, is composed of mullite needles with interstitial siliceous glass, the same as refractories made from andalusite. This porcelain is a very satisfactory refractory to support the platinum winding of an electric furnace. There is no reaction between the refractory and the platinum. At the Geophysical Laboratory there are furnaces built in this manner that have been in use for years.

R. TWELLS, JR.:[1] The development of andalusite as a refractory has progressed considerably since the presentation of this article in February. As car top blocks for the Harrop kiln cars, the andalusite is very good. Whereas the fire clay brick or blocks tend to shrink and warp badly on repeated firings through the kiln, the andalusite blocks hold their size and shape exceptionally well, nor do they tend as readily to vitrify and crack.

For refractory uses at about cone 18 it has been found desirable to add a small percentage of plastic kaolin to the andalusite to facilitate molding. As was stated in the article, it is readily possible to mold a 100% andalusite mix; however in production on a larger scale the additional bond gives added strength and reduces the loss in the green state.

Some good results are being attained at cone 18 with andalusite saggers having the lower halves of the bottoms made from silicon carbide. The thin layer of silicon carbide acts as a reinforcement to help support the weight of the ware. Contrary to what would be expected, the andalusite and silicon carbide bond together fairly well in this way. Some of these saggers have been through the tunnel kiln 10 times and are still in fair condition. The andalusite sides seem to resist cracking better than the regular silicon carbide saggers. For use as a sagger for temperatures about cone 10 it would be unnecessary to use a reinforcement of silicon carbide. The experience at the Champion Porcelain Company with some mixtures containing about 50% andalusite and 50% plastic kaolin would indicate that similar combinations would have very good lives as saggers at the temperatures used in most whiteware plants.

The Research Department of the Champion Porcelain Company is now working on some extensive experiments to study the characteristics of andalusite products under different conditions. The results of this detailed work will no doubt be made available later.

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[1] Recd. June 1, 1925.

FUNDAMENTALS OF HEAT FLOW IN MOLTEN GLASS AND IN WALLS FOR USE AGAINST GLASS[1]

By George V. McCauley

ABSTRACT

This paper deals with the flow of heat through molten glass and through glass retaining clay walls. Reference is given to previous work on heat flow by convection, radiation and conduction as applied to clay refractorise. Experimental data are given for *conductivity of flux block*, and for the *effective conductivity of molten glass* as a function of temperature. Photographs are presented to show *existence of convection currents in a glass tank*.

Introduction

Method of Analysis In considering the heat flow through molten glass and retaining clay walls, it is often customary to regard the problem as analogous to the flow of electricity through a series of conductors of different resistances. Thus temperature difference becomes analogous to difference of potential and quantity of heat per unit of time, analogous to current. The quotient of temperature difference by quantity of heat per unit of time then corresponds to thermal resistance. It is further customary to use such units as will express quantities of heat in watt seconds or watt hours. This method while simple in theory has its limitations when one wishes to express by means of curves, the flow of heat as a function of temperature existing in the glass, refractory and outside air. The reason for these limitations is that the thermal resistance factor is too often a complex function of the temperatures themselves and not of the temperature difference or thermo-motive forces involved. Therefore in our discussion we shall employ the older method of analysis and divide the problem into heat flow by conduction, convection and radiation. From this viewpoint very little can be added to the excellent treatment of Professor Trinks in his book on "Industrial Furnaces."

I. Heat Flow in Tank Blocks

Heat Flow from Outside of Block At the outside surface of a tank block a definite temperature of equilibrium is established depending upon the inside tank temperature, the velocity and temperature of outside cooling air, and the thermal conductivity of the block. Assuming a temperature of Θ_0 for this outside block temperature and a temperature of Θ_a for the cooling air, a definite heat flow passes from the block to the air. This flow takes place by convection, radiation and possible conduction through a thin layer of air.

Heat Flow by Convection A number of experimenters from Newton's day to the present have sought to establish the relation between heat flow by convection, both natural and forced, and the temperature difference between solid body and moving fluid. Everyone, of course, is familiar with the statement of Newton's law of cooling. Boussinesq[1] from theoretical considerations showed that heat loss by convection is directly proportional to the temperature difference between surface and moving fluid. Rayleigh[2] also shows this from dimensional analysis or principle of similitude. This has been verified in the case of cylindrical bodies at least, by King[3] and others.

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[1] Presented at the Annual Meeting, Columbus, Ohio, Feb. 1925. (Glass Division.)

For natural convection, Lorentz[4] gives us the theoretical law for convection at a flat vertical surface. This states that heat loss is proportional to the five-fourths power of the temperature difference between plate surface and moving air. This is in agreement with the empirical formula developed by Dulong and Petit[5] and has since been verified by the work of Langmuir[6] and of the National Physical Laboratory.[7]

The results of these investigations from theoretical considerations and experimental verification, show that for a given velocity of air, heat flow by convection is proportional to the five-fourths power of the temperature difference between solid surface and moving fluid. The dependence on velocity has not been so firmly established although the later experiments especially of Langmuir, indicate a heat flow proportional to the velocity for a given temperature difference between surface and moving air. Combining the work of Wamsler,[8] who finds the convection loss from rough surfaces to be approximately 90% of that from smooth surfaces, with that of Langmuir as done by Professor Trinks[9] we may express flow of heat by convection in still air by the relation

$$Q_v = .25\,(\Theta_0 - \Theta_a)^{5/4} \qquad (1)$$

where Q_v denotes the quantity of heat in B.t.u. flowing per hour per square foot of surface from the block into the surrounding air by convection alone. The term "convection" is here used to denote the complete manner of heat flow from block surface to air other than that accounted for by radiation. Heat flow by radiation is known to take place in accordance with the laws of Kirchhoff and of Stefan-Boltzman. Thus the quantity of heat flowing by radiation from a unit area of surface at temperature Θ_0 per unit of time to a surrounding absorbing medium at temperature Θ_a is given by

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[1] *Comptes Rendus*, **133**, 257 (1901).

[2] *Nature*, **95**, 66 (1915).

[3] *Phil. Trans., R. S.*, **214**, 373 (1914).

[4] *Ann. der Phys.*, **13**, 582 (1881).

[5] *Ann. d. Chim. Phys.*, **7** (1817).

[6] *Trans. Am. Electrochem. Soc.*, **23**, 299 (1913).

[7] Report on "Heat Transmission by Convection and Radiation," published by the Food Investigation Board (1921).

[8] *Zeits. d. V. D. I.*, p. 599 (1911).

[9] "Industrial Furnaces," p. 63.

$$Q_r = Ak_r \{(\Theta_0 + 460)^4 - (\Theta_a + 460)^4\} \qquad (2)$$

where A denotes the absorbing power of the block surface to black body radiation and k_r is the total radiation constant expressed in B.t.u. per square foot per hour from a surface at 1 °F absolute to a medium at 0° absolute. The constant A is likewise the factor of proportionality by which we need multiply black body radiation to give the radiation of a body at the same temperature as the black body and whose absorption coefficient is A.

The constant k_r has been determined by a great many investigators and the present adopted value of 5.46×10^{-12} watts/cm.²/deg.⁴ becomes 1.64×10^{-9} in our units of B.t.u. per hour per square foot per °F.⁴

For the constant A, Wamsler finds the value .96 for rough wrought iron surface; and this is also probably quite applicable to clay block surfaces.

Assuming this value for the absorption coefficient of clay block and combining the expression of heat flow by radiation and convection we have

$$Q_s = 1.57 \times 10^{-9} \{(\Theta_0 + 460)^4 - (\Theta_a + 460)^4\} .25 (T_0 - T_a)^{5/4} \qquad (3)$$

By means of this relation it is now possible to compute for various air temperatures, the total heat flow per hour per square foot from a block surface as a function of the temperature of this block surface. Such curves are shown in Fig. 1.

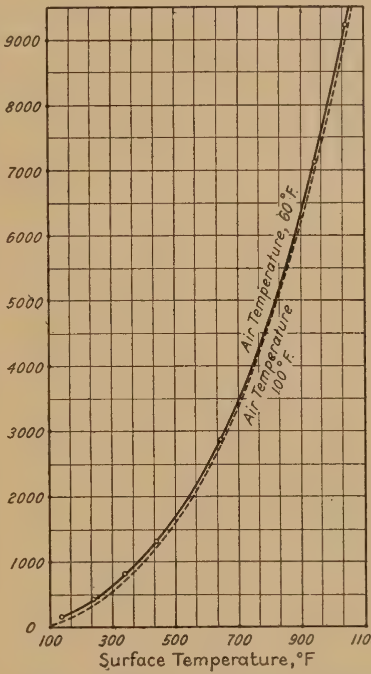

FIG. 1.—Flow of heat by radiation and convection from rough vertical surface. Heat flow (B. t. u. per sq. ft. per hr.).

Heat Flow by Conduction

The same quantity of heat which flows per hour per square foot from the block to the surrounding air must also pass in the same time per square foot through the block. The passage here, however, is by conduction. In the majority of cases, the problem is one of the simplest in heat conductivity. The flow is in one direction only, and can usually be regarded as independent of time. The flow is thus said to be linear and steady. The flow under these conditions is given by the relation

$$Q_c = \frac{k(\Theta_1 - \Theta_0)}{L} \tag{4}$$

Q_c denotes the heat flow by conduction in B.t.u. per square foot per hour, where k is the coefficient of thermal conductivity, L is the thickness in inches and Θ_1 and Θ_0 are the temperatures of hot and cold surfaces of the block respectively.

Practical Application Since the heat flow as given by relations (3) and (4) are identical we may combine the two to help us predict any one of three things connected with the heat flow through the block. If we can measure the two surface temperatures of the block, we are in a position to compute the value of k, the thermal conductivity of the block. This may prove of assistance when properties of several blocks are desired. If we know the conductivity coefficient and the inside block temperature, we can find the outer surface temperature. This we find useful in designing furnaces to operate at certain inside temperatures and we wish to know what temperature we may expect on the outer surface of the block. In this form, it is also useful in computing what wall thickness, or equivalent wall thickness secured by insulation that is required to keep the heat loss down to a certain prescribed value. The third way in which the above relation is useful is that in which the conductivity and the outer surface temperature are known. In this case, we may compute the inner surface temperature, and hence arrive at an approximate value of the glass temperature at this point in the tank.

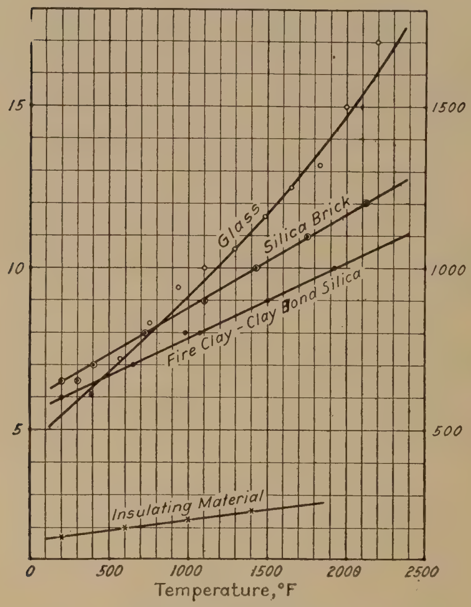

FIG. 2.—Conductivity of refractories. Conductivity, B.t.u. per sq. ft. per hr. per ° F. per in.

Before we can make these last two computations of block temperatures, however, we must have measurements of the conductivity of the block. Direct observation on this particular material seem to be lacking, although numerous workers have made measurements of the thermal conductivity of other refractory bodies. Indeed the work is so abundant and the results so numerous that one in his bewilderment knows not which value to choose for his particular case.

I do not wish to imply that these measurements are all wrong. On the contrary, they doubtless represent variations due to intensity of heat treatment, porosity, age and composition of the refractories studied together with certain differences due to methods of experimental procedure. It would certainly be worth while and at the same time afford a pleasant research to determine exactly the influence of these various factors on thermal conductivity and to further establish a method of classifying refractories by which one would be able to select the proper value for his particular case. At present perhaps we can do no better than Professor Trinks[1] has done. He gives in his book mean value curves taken from a large group of measurements of these thermal conductivities for fire clay, silica brick and insulating brick. These are shown in Fig. 2.

Determination of Heat Conductivity of Flux Block

A few years ago the writer wishing to compute the flow of heat through a flux block wall was at a loss to know what value of thermal conductivity to use. A series of measurements were made, therefore, with a water calorimeter on a small oil-fired furnace. The furnace was blocked with 3-inch flux material and the measurements were made in the center of the bottom where the flow of heat was linear. Temperatures were measured with thermocouples of fine copper-constantin and platinum-platinum-rhodium wires. These couples were inserted in small holes drilled edgewise into the block at various known distances from its surfaces and on the surface of the block above the calorimeter. Temperature changes in the calorimeter were obtained by two copper constantin couples reading differentially. Water was supplied to the calorimeter from a constant pressure reservoir.

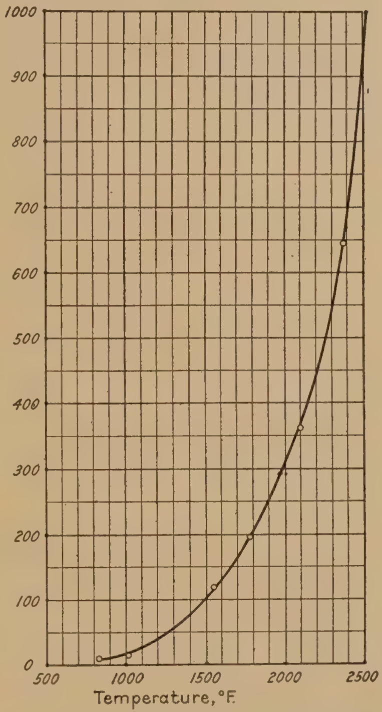

FIG. 3.—Effective conductivity of glass. Conductivity, B. t. u. per sq. ft. per hr. per °F. per in.

Results Obtained The results of this investigation are shown in Fig. 2 by way of comparison with the mean value curves given by Professor Trinks for other refractories. It is to be observed that the results agree fairly well with those of silica brick and fire clay at lower temperatures. The tendency to increase with temperature appears to be more pronounced, however, in the case of the flux material. Since only one flux batch was studied, it is not to be assumed that the values for others will agree any more closely with these than do those of other refractories with one another. For the present, however, until a more exhaustive study has been made we can do no better than make our computations with these values.

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[1] *Op. cit.*, p. 67.

Computing Inside Block Temperature

Having determined the conductivity coefficient, a single example will illustrate the use of the curves in Fig. 1 together with relation (4) above in computing the inside block temperature when the outer surface temperature is known.

Let us assume an outside surface temperature of 400°F on the face of a 12-inch block. If there is no artificial cooling of the blocks, we find from Fig. 1, the heat flow from a surface at 400°F to a room temperature of 60°F to be 1120 B.t.u. per square foot per hour.

Since the conductivity of the block varies with the temperature, we must assume an inside block temperature in order to find from Fig. 2 an approximate value of the conductivity to use. Let us then assume an inside temperature of 1800°F and then from Curve II we get a mean conductivity of 9.9 between 400 and 1800. Substituting these in relation (4) above we have

$$Q = 9.9 \frac{(1800 - 400)}{12} = 1150 \frac{\text{B.t.u.}}{\text{ft.}^2\ \text{hr.}}$$

But from Fig. 1 we see that a block at 400° outside temperature is only giving up 1120 B.t.u./ft.^{2} hr. Consequently our assumption of 1800°F for the inside block temperature is a trifle too high. A second approximation will usually result in a correct solution.

II. Heat Flow through Molten Glass

In the flow of heat through the molten glass all three processes of heat flow are in operation. Some heat is passed on from layer to layer by conduction, just as in the case of the block. Another portion is bodily carried by the movement of glass from places where the mean temperature in a vertical column is high to places where it is low; and finally a third portion is radiated from hot layers of glass to colder ones below. Since the glass is partly transparent to its own relations heat may be transmitted readily through it. This property of course depends upon the nature of the glass in question.

No data is available as to the relative magnitudes of the flow of heat in glass by these three processes. Indeed it would require careful experimentation to distinguish between them. One would be obliged to first determine the conductivity and radiation coefficient combined by experimenting in a tall narrow column of glass where convection was eliminated. Then the radiation constants would be determined by measuring the transmission and absorption factors for various temperatures. With these two observations and by measuring temperature and total heat flow in the tank we could, by difference, find the influence of convection.

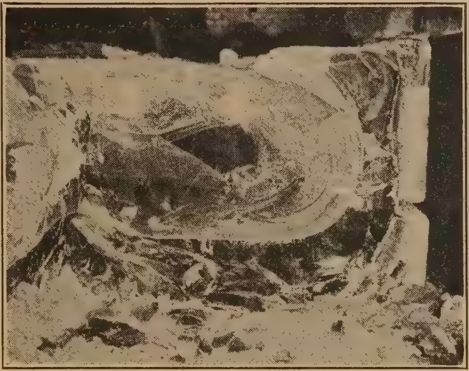

Fig. 4.

Fig. 5.

Determination of Heat Flow through Molten Glass

Some time ago the writer carried out in part the last of these three steps. This work was done in the same furnace in which conductivities of flux block were studied. The glass studied was a non-lead bulb glass. The total depth of glass was twelve inches. Measurements consisted of merely obtaining temperature gradients simultaneously in the glass and in the blocks. The ratio of these respective gradients is taken as the ratio of the effective conductivity of molten glass to that of flux block in contact with the glass. Having previously measured the latter for various temperatures, the effective conductivity of molten glass may be computed and plotted as a function of temperature. This relation is shown in the curves of Fig. 3.

Difference in Effective Conductivity of Block and Glass

It is rather striking to observe the great difference between the effective conductivity of molten glass and the conductivity of block material. Also the rapid increase in this effective conductivity is worthy of note. A glance at the curve shows us that heat flows through the molten glass at 2500°F some seventy-five times faster than it can pass through the block. If then the temperature gradient in the block is 175°F per inch, we will have in the glass near the surface, where the temperature is approximately 2500°F, only about $2^1/_2$°F change in temperature per inch depth in the glass. This difference of course, increases as the distance from the surface of the glass increases; but even at the very bottom of the pool of molten glass, the conductivity is considerably greater than it is for the block. Because of this high effective thermal conductivity of the molten glass it is possible to keep the glass in the molten state at a depth of three or even five feet by the application of heat at the surface.

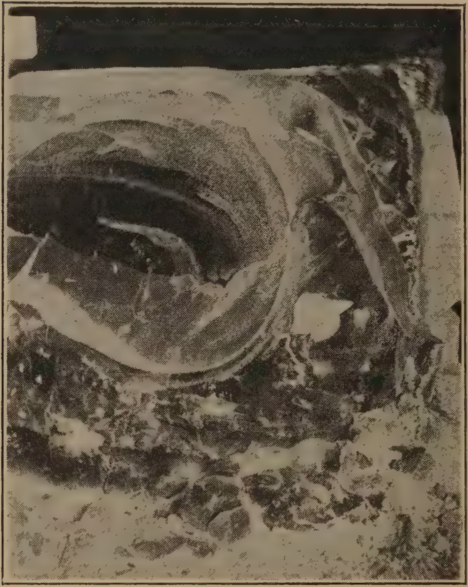

Fig. 6.

Analysis of High Heat Conductivity of Glass

To say what part of this effective conductivity is due to radiation, what part to convection and what part represents a true conductivity would be mere speculation at the present time. We can, however, say with certainty that convection increases with temperature or fluidity and, in all probability, transmission to radiation decreases. The true conductivity may or may not increase with temperature, but in view of the fact that the effective conductivity which we have measured increases so rapidly with temperature, even at those temperatures where fluidity and hence convection is not great, one is fairly justified in saying that even the true thermal conductivity increases with temperature, as it does for refractory materials.

Physical Evidence of Convection in Glass

It might be well, while speaking of convection in molten glass, to present some evidence of its occurrence as well as of its magnitude. The ac-

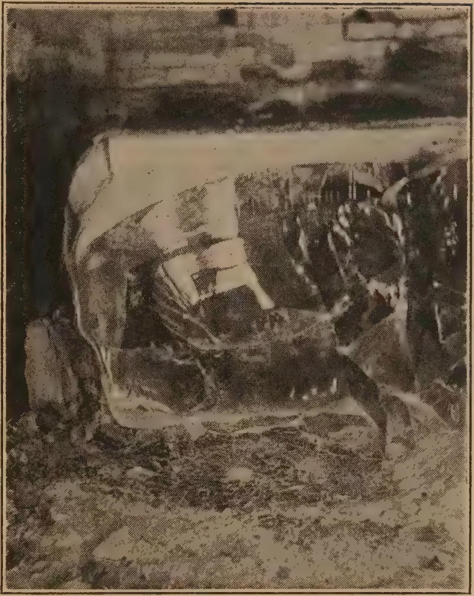

FIG. 7.

companying photographs were made about three years ago to determine as far as possible, the movement of glass in a tank. They represent conditions in a Pyrex tank after a run of approximately fourteen months. To obtain these photographs the tank was filled and worked to a normal rate until the actual time of letting out the fires. The tank was then cooled rapidly to freeze the glass in the position occupied while working. Of course, some motion must have occurred before the glass froze. Glass moved forward into the working end to establish static equilibrium after the pull of the shops ceased. Convection also must have continued for a while. The photographs are, however, as near as can be obtained of what the glass is doing while the tank is in operation.

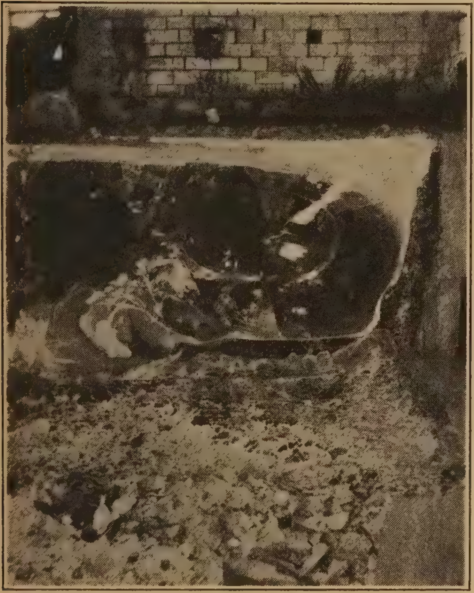

FIG. 8.

Beginning at the bridgewall and working back toward the doghouse, the glass was removed in sections of two or three feet across the tank to the full depth of the glass. As the work progressed photographs were taken.

A layer of scum consisting largely of cristobalite covered this tank and by this the convection was traced. This material, being lighter than the glass, floats on the surface and as convection from the hot center to the side walls takes place, a tendency exists to carry this scum to the walls and down to the bottom along which it returns to the central column. The combined forces of convection and gravity on this layer make it thickest at these walls and thinnest at the center. Some, however, is carried down with the convection stream in spite of gravity and affords a trace by which the force of convection is traced after the glass is frozen.

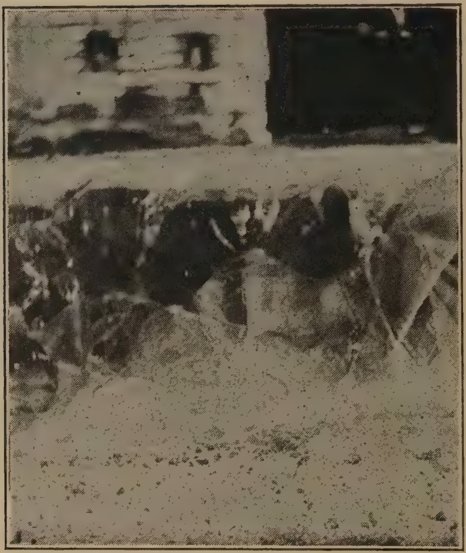

Fig. 9.

Figures 4 and 5 show the transverse convection at a point about two thirds the distance from doghouse to bridgewall. It is also to be observed that the erosion contour of the block conforms to the convection stream especially at the bottom of the tank. The surface erosion is generally affected also by other forces such as changes in surface tension of the glass caused by the solution of block material therein.

Similar effects are shown in Figs. 6 and 7. These were taken at a point about one-third the distance from doghouse to bridgewall. In Fig. 6 we see evidence of motion very near to the side block, the lower course of which is still in place.

In Figs. 8, 9, 10 and 11 we have the combined effect of transverse convection to the side walls and a longitudinal convection to the rear wall.

Figure 12 indicates that a fair temperature must have existed even on the bottom of the tank directly under the filling door to cause iron (for such is the composition of the cross) to melt and run together in one solid mass filling the cracks between these blocks.

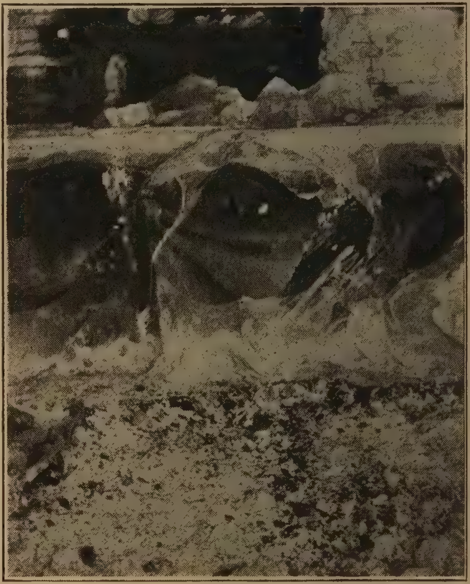

Fig. 10.

Velocity of Convection Currents in Glass

To secure some idea of the velocity of these convection currents, drops of colored glass were dropped into the center of the small tank in which conductivity experiments were being carried out. After dropping in the colored glass, the temperature was maintained for two hours, and then the fires were turned off to cool quickly. This experiment was made at temperatures of 1830°F and 2550°F. The glass was then cut out and the trace of the coloring matter observed. In the case of the lower temperature, there had resulted a movement of barely 18 inches while at the higher temperature, the coloring trails could be traced for one complete revolution to the corner of the tank down the side block across the bottom and back up the center giving in all a distance of at least six feet or a velocity of 3 feet per hour. Observations made on the movement of batch in a commercial tank melting the same bulb glass showed a surface velocity toward the cold rear corner of approximately eighteen feet per hour when the tank temperature was in the neighborhood of 2500°F. It might be emphasized in passing that this motion was in opposition to the gas current existing between ports at the time.

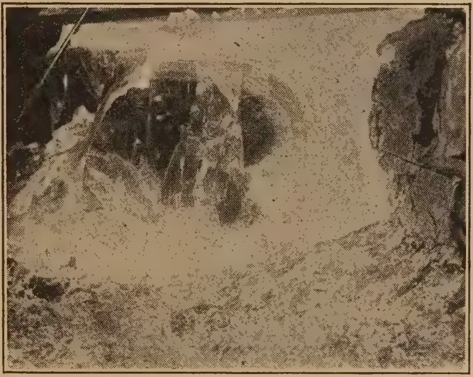

FIG. 11.

These photographs and observations are evidence of the existence of motions in molten glass that no doubt play a large part in the transfer of heat, in block erosion, and in fact on the glass quality itself. As this is primarily a discussion of heat flow, we will not consider these other effects, however interesting and important they may be.

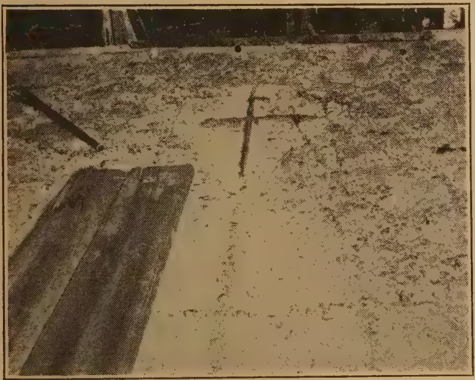

FIG. 12.

Heat Flow as Influenced by Convection

Effective conductivity of molten glass was taken to be a property inversely proportional to the temperature difference between two points in the glass and unless convection is a perfectly definite function of this same temperature difference, we may find different effective thermal conductivities for given temperatures, depending upon the magnitude of these convection currents. This is a matter for further research to decide.

Our data at present is too meager to say whether heat transfer by convection follows an analogous law to that expressed by Lorentz and Rayleigh; for the heat loss from vertical walls cooled by air currents. According to this law heat would be supplied by convection alone to the block in proportion to the five-fourth power of the temperature difference between glass and block and in inverse proportion to the one-fourth power of the viscosity of the glass. But whether or not a definite temperature gradient is established through a given depth of glass in a tank maintained at a given surface temperature, as is assumed in the computation of effective conductivity above, it is quite possible that this gradient may be changing locally due to disturbance of temperature distribution causing new convection currents or changes in direction of old ones. These effects seem to the writer to be more plausible reasons for fluctuations observed in the glass temperature of a tank rather than changes in gas pressure as reported in the January, 1925, number of *Ceramic Industry*.

Corning Glass Works
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THE DENSITY AND INDEX OF REFRACTION OF GLASS VERSUS ITS COMPOSITION[1]

By A. N. Finn and H. G. Thomson

ABSTRACT

A study of the available data on the relations between density, refractive index, and composition of glasses of the soda-lime series leads to the conclusion that these relations can be adequately expressed by formulas of the type $d = a(p + c)^b$, in which a, b and c are constants and d is that part of the total density of the glass due to p per cent of any constituent oxide. The results obtained for density are more satisfactory and can be applied over a much wider range than those computed by the well-known equation of Winklemann and Schott.

Introduction and Historical

The relations between the physical properties and chemical composition of any substance have always been subjects of interest and much thought has been given to the evaluation of these relations by the scientific and technical world. Glass has not been overlooked in this connection, as is evident from a study of the literature.

In connection with the work on glass which is being done at the Bureau of Standards, it seemed desirable to study the data reported by different investigators to see if they might not yield more satisfactory relations than those previously found.

Winklemann and Schott[2] published their first work on the relations between composition and physical properties of glass in 1893. Later Larsen,[3] Tillotson,[4] Peddle,[5] Baillie,[6] and English and Turner[7] added their contributions to the subject.

The conclusions reached by these investigators are in general based on the assumption that the density of glass can be regarded as a linear function of the relative amounts of its constituent oxides which is expressed by the equation $\frac{100}{D} = \frac{p_1}{d_1} + \frac{p_2}{d_2} + \frac{p_3}{d_3}$. In this equation D is the density of the glass, p_1, p_2, p_3 are the percentages of its constituent oxides, and the coefficients d_1, d_2, d_3 are the apparent densities of the corresponding oxides.

Winklemann and Schott state that the relations derived by them are only applicable to glasses very similar in composition to those from which the values of d were obtained and that for glasses of different composition the relations are not so satisfactory. Although the others do not make such a statement, a study of their results leads to the same conclusion, and the values they report for apparent densities, or "factors" as they are called, vary with the types of glass from which they were derived. The factors recommended by various investigators are given in Table I.

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[1] Published by permission of the Director of the United States Bureau of Standards, Department of Commerce. Presented before the Glass Division of the American Ceramic Society at Columbus, Ohio, February, 1925.

[2] *Ann. d. Phys. and Chem.*, **1893, 1894, 1897.**

[3] *Am. J. Sci.*, **28**, 263 (1909).

[4] *J. Ind. and Eng. Chem.*, **3**, 897 (1911); **4**, 246 (1912).

[5] *Jour. Soc. Glass Tech.*, **1920, 1921, 1922, 1923.**

[6] *Jour. Soc. Chem. Ind.*, **40**, 141 (1921).

[7] *Jour. Soc. Glass Tech.*, **1920, 1921, 1922, 1923.**

TABLE I

GENERAL EQUATION AND FACTORS FOR SEVERAL OXIDES RECOMMENDED BY SCHOTT (S), TILLOTSON (T), BAILLIE (B), AND ENGLISH AND TURNER (E. & T.)

$$\frac{100}{D} = \frac{p_1}{d_1} + \frac{p_2}{d_2} + \frac{p_3}{d_3} + \ldots\ldots$$

	S	T	B	E. & T.
SiO_2	2.3	2.30	2.24	2.20
Na_2O	2.6	2.60	3.20	3.47
CaO	3.3	4.10	4.30	5.00
MgO	3.8	4.00	3.25	3.38
Al_2O_3	4.1	2.75	2.75	2.75

Peddle did not derive a series of factors, but states: "The assumption that the density of glass can be calculated from the densities of the constituent oxides is in error, and the equation of Winklemann and Schott for the calculation of density is of no use where 'extreme' glasses are concerned, that is, glasses containing an abnormal amount of any constituent oxide."[1]

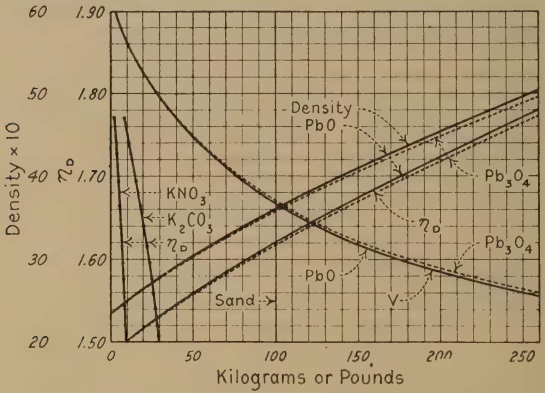

FIG. 1.—Batch composition diagram for the series of ordinary flint glasses. The diagram is prepared on the basis of sand 100. From the diagram the approximate batch composition for any flint glass of given refractive index, n_D, or V-value, or density, d, can be read off directly.

General

If the changes in the density of glasses of different composition are plotted against changes in composition on rectangular coördinate paper, the graph is almost invariably a curve and not a straight line which would be required by the Schott equation. This is well illustrated by the diagram prepared by F. E. Wright,[2] by means of which he shows the relations between composition, density, index of refraction, and dispersion of optical glasses of the lead series (Fig. 1).

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[1] *J. Soc. Glass Tech.*, **4,** 8 (1920).

[2] "The Manufacture of Optical Glass and Optical Systems," p. 101.

Since these curves and other available data show gradual changes in the properties of glass with small variations in composition and do not, in any range, show a rapid change in slope which might be expected if there were changes in molecular constitution, it is safe to assume, for the purpose of this work, that changes in the density of glass are continuous functions of the relative amounts of its constituent oxides.

This assumption might lead to the conclusion that glass is a homogeneous mixture of its constituent oxides and devoid of molecular combination. Such a conclusion is not necessarily true, as it may safely be stated that the observed density and also index of refraction are the results of averages of mixtures of compounds which have not been allowed to assemble in groups of sufficient size to permit their detection or identification.

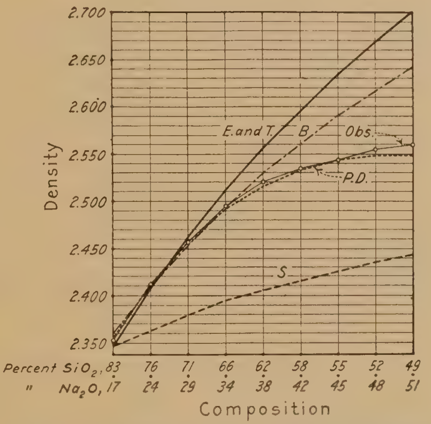

FIG. 2.—Comparison of observed densities (obs.) of silica-soda glasses and densities computed by English and Turner (E. and T.), Baillie (B), Schott (S) factors, and the "partial density" method (P. D.).

Silica and Soda

The work reported in this paper is based largely on the results obtained by Peddle,[1] who made a series of silica-soda glasses varying in composition from approximately 83% silica and 17% soda to 50% each of silica and soda. The density of these glasses varied from 2.353 to 2.560.

Assuming that the change in density is a function of the change in the percentages of silica and soda, it was found that the relation could be quite accurately expressed by an equation of the form $d = a(p + c)^b$ in which d is the "partial density" or that part of the density of the glass that might be attributed to either of the constituent oxides, p is the percentage of that oxide and a, b and c are empirical constants which have the following values:

Oxide	*a*	*b*	*c*
SiO_2	0.3325	0.4463	—30
Na_2O	0.01869	1.081	0

The density, D, of the nine silica-soda glasses reported by Peddle is the sum of the partial densities of the silica and soda and may be computed from the equation

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[1] *J. Soc. Glass Tech.*, **4**, 6 (1920).

$$D = 0.3325\,(p - 30)^{0.4463} + 0.01869\,(p)^{1.081}$$

with a maximum difference of less than 0.25% (or 0.006 actual density) between the computed and observed values except for the 50-50 glass, in which case the difference is 0.43% (0.011 actual density). Figure 2 shows the observed values, which are represented by circles, the values obtained by computing the densities of this series of glasses by the "partial density" method and by the Schott equation using the factors recommended by English and Turner, Baillie, and Schott, and also the composition of the glasses considered.

It is evident from Fig. 2 that Schott's statement regarding "similarity" of glasses is correct, for although the differences are not great in the high silica region, they become much greater as the silica content decreases and reach maxima of —4.5% (—0.117) and +5.5% (+0.141) when the silica-soda ratio is 49:51.

Lime

Using the equations obtained for silica and soda, the partial densities of these constituents were computed for the twelve silica-soda-lime glasses discussed by Peddle[1] and the difference between the sum of these and the observed density of the glass was considered the partial density due to lime. These values are given approximately by the equation

$$d = 0.03365\,(p)^{0.9887}$$

The maximum difference between the observed density of any of these glasses and the density obtained by adding the partial densities computed from the equations for silica, soda and lime was 0.72%. Substitution of the Baillie and English and Turner factors in the Schott equation gave maximum differences of 1.0% and 3.3%, respectively. These results are shown in Fig. 3.

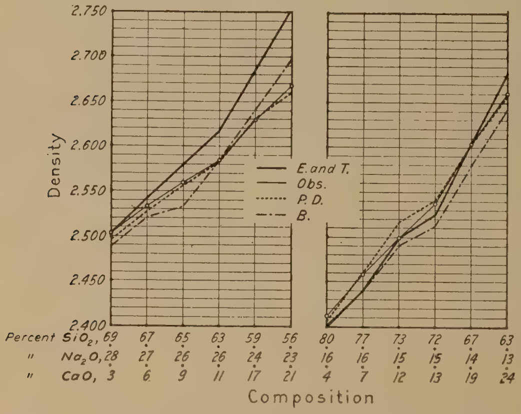

FIG. 3.—Comparison of observed densities (obs.), of silica-soda-lime glasses and densities computed by English and Turner (E. and T.), and Baillie (B) factors, and the "partial density" method (P. D.).

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[1] *Jour. Soc. Glass Tech.*, **4**, 76 (1920).

In applying these equations to a series of seventeen soda-lime glasses reported by English and Turner,[1] satisfactory agreement was not obtained between the computed and observed densities. Although the maximum difference was 0.72%, as it was in the case of the Peddle glasses of this type, the other values did not agree as well as in the previous case. However, by proceeding with the English and Turner glasses as in the case of the Peddle glasses, somewhat different constants were obtained for the lime equation as indicated below:

Glass made by	Constants for lime equation *a*	*b*	*c*
English and Turner..	0.02813	1.035	+0.2
Peddle.............	0.03365	0.9887	0.0

The use of this modified equation for the partial density of lime gave a maximum variation of 0.28% (0.007) as compared with 0.9% (0.023) obtained by the English and Turner factors, and again this relatively large difference was obtained when the composition changed materially. (The silica content changed from 74% to 66% with a corresponding increase of the lime.)

The need for different constants in the lime equation, which are required to satisfy the data, may be due to several uncertain conditions among which may be mentioned (1) the actual compositions of the glasses considered, (2) the degree of annealing,[2] and (3) variations in temperature at which the densities were determined,[3] assuming that all samples were free from bubbles or seeds.

The compositions of the glasses reported by Peddle could only be obtained from batch compositions as no analyses were reported, and certainly some change will always be produced by volatilization of certain constituents and by solution of the clay from which the melting pots were made. The compositions of the English and Turner glasses were obtained by chemical analysis and hence are probably more reliable.

Peddle does not state the degree of annealing for his glasses nor the temperature at which densities were determined, while English and Turner emphasize the necessity of using only well annealed glass and state that the densities of their glasses were determined at 20°C. However, Peddles' glasses were cooled in the melting furnace and it is not thought that they were highly strained, although they were probably not well annealed.

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[1] *Jour. Soc. Glass Tech.*, **3**, 126, 227 (1919); **4**, 127 (1920). The composition of these glasses varied as follows: silica, 66–75%, soda 11–25%, lime 0.2–18%.

[2] Tool and Eichlin have shown that in some glasses the density may be decreased as much as 1% by rapid cooling from the maximum annealing temperature (*J. Opt. Soc. of Am.*, **8** [3], 437 (1924).

[3] Neglecting the thermal expansion of glass, a glass whose density at 4°C is 2.50 will have an apparent density of 2.5025 at 15°C and 2.5050 at 20°C or a difference of 0.1% between 15° and 20°C.

Magnesia and Alumina

Following the same method of computation as used in obtaining the values of a, b and c in the partial density equation for lime, and using the data on the soda-magnesia and soda-alumina glasses made by English and Turner[1] the following constants were obtained for the partial density equations of magnesia and alumina:

Oxide	a	b	c
MgO	0.3017	0.9262	0
Al_2O_3	0.00675	1.3571	+3

Using these constants for determining the partial density of magnesia, the maximum difference between the computed and observed densities of the soda-magnesia glasses is 0.2% (0.005), whereas the English and Turner factors give 0.66% (0.016) and the Baillie factors give 0.25% (0.006), which is a better agreement for the "factor" method than was obtained for the soda-silica or soda-lime-silica glasses.

The constants for determining the partial density of alumina are not very satisfactory and although they will be briefly referred to again in this paper, a more complete discussion will be presented in a future paper on this subject.

Index of Refraction

A method of reasoning similar to that used in considering the effects of changes in composition on density was applied to index of refraction. This led to a similar series of equations in which the constants for the "partial index of refraction" (n_d) due to silica, soda and lime are as follows:

Oxide	a	b	c
SiO_2	0.03875	0.8063	−10
Na_2O	0.01406	1.0193	0
CaO	0.01332	1.069	+ 1

Using these constants in the equations $N_d = n_{d_1} + n_{d_2} + n_{d_3} + \ldots\ldots$ and $(n_d)_x = a(p_x + c)^b$, the computed indices of refraction of the soda-silica glasses varied less than 0.001 from the observed indices if the soda did not exceed 30%, and the computed indices of five soda-lime glasses[2] made and analyzed at the Bureau of Standards varied less than 0.005 from the observed values. These values are not as good as those obtained by Tillotson,[3] who determined K (specific refractive power) in the Lorentz equation, using values of d obtained by substituting his own factors for apparent density in the Schott equation.

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[1] *Jour. Soc. Glass Tech.*, **4,** 155 (1920); **5,** 277 (1921).

[2] Approximate composition of these glasses was: silica 75%, soda 13% and lime 12%.

[3] *Jour. Ind. and Eng. Chem.*, **4,** 246 (1912).

Results Obtained by Extrapolation

It is exceedingly interesting to note the results obtained by computing the densities and indices of refraction at 100% for the oxides discussed in this paper (see Tables II and III). The silica equations at 100% (in other words, pure silica) give a density of 2.214 and an index of refraction (N_d) of 1.4587, an excellent agreement with the observed values for fused silica which are, according to Larsen, 2.213 and 1.4590.

The lime equations at 100% give a density of 3.195–3.310 and an index of refraction of 1.8516. The reported densities of pure lime vary from 3.08 to 3.30 and the index of refraction varies from 1.725–1.83. In this connection attention is directed to the fact that although the computed index of refraction of lime is higher than that given for crystallized lime, this is consistent with the fact that in those crystalline minerals which contain high percentages of lime and can also be obtained in the form of glass, the index of refraction of the glass is higher than that of the crystal and since, in general, an increase in refractive index is accompanied by an increase in density, it follows that the density of similar lime compounds might be higher in the glass than in the crystal. This might be interpreted as an indication that lime undergoes a molecular contraction when

TABLE II

"PARTIAL DENSITY" EQUATIONS AND VALUES OF *a*, *b* AND *c* FOR SEVERAL OXIDES. ALSO, COMPUTED DENSITY FOR 100% OF EACH OXIDE AND THE OBSERVED DENSITY

$$D = d_1 + d_2 + d_3 + \ldots\ldots$$
$$d_x = a(p + c)^b$$

				100%	
	a	*b*	*c*	Comp.	Obs.
SiO_2	0.33250	0.4463	—30.0	2.214	2.213
Na_2O	0.01869	1.0810	0	2.715	2.550
CaO[1]	0.03365	0.9887	0	3.310	3.08–3.33
CaO[2]	0.02813	1.0350	+0.2	3.195	3.08–3.33
MgO	0.30170	0.9262	0	2.148	3.47–3.64
Al_2O_3	0.00675	1.3571	+3.0	3.640	3.850

TABLE III

EQUATIONS AND CONSTANTS FOR DETERMINING INDEX OF REFRACTION (N_d) OF SILICA-SODA-LIME GLASSES. ALSO, COMPUTED INDEX FOR 100% OF EACH OXIDE AND OBSERVED INDEX

$$N_d = (n_d)_1 + (n_d)_2 + (n_d)_3 + \ldots\ldots$$
$$(n_d)_x = a(p + c)^b$$

				100%	
	a	*b*	*c*	Comp.	Obs.
SiO_2	0.03875	0.8063	—10	1.4587	1.4585
Na_2O	0.01406	1.0193	0	1.5369	
CaO	0.01332	1.0690	+1	1.8516	1.725–1.83

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[1] From SiO_2–Na_2O–CaO glasses reported by Peddle.

[2] From SiO_2–Na_2O–CaO glasses reported by English & Turner.

present in glass, but it may also indicate that lime in a glass produces a greater contraction or condensation of one or more of the other constituent oxides which, by the method of computation used, would not be attributed to those oxides but would be attributed entirely to the lime and hence produce relatively higher values for it.

The value obtained for the density of magnesia at 100% is 2.148. This is much lower than any reported values for the density of pure magnesia[1] which vary from 3.47 to 3.64, but this low computed value is consistent with the fact that the magnesia glasses have lower densities than glasses in which it is replaced by lime.

The value computed for pure alumina, 3. 4, indicates that it should produce a greater increase in the density of a glass than either lime or magnesia, but, as a matter of fact, its effect is similar to magnesia, *i. e.*, it produces a glass of lower density than one containing a corresponding amount of lime.

It must be borne in mind, however, that the range of compositions on which these conclusions are based varied considerably. The percentage of silica varied from 50–85%, soda 15–50%, lime 3–24%, magnesia 1–10%, alumina 3–13%, and the extrapolation of values from 10% or 20% to 100% may not be justified and this the more because the actual composition of all the glasses considered is not definitely known and the validity of the initial assumption on which the arguments are based has not been definitely established.

Conclusions

In conclusion it may be stated that the density of the glasses of the silica-soda-lime series and also some others may be computed with greater accuracy and over a wider range of compositions than by any previously reported methods.

The relations deduced are expressed by the equations

$$D = d_1 + d_2 + d_3 \text{ and}$$
$$d_x = a(p + c)^b$$

in which D is the density of the glass, d_1, d_2, d_3 are the partial densities due to the constituent oxides, p is the percentage of the corresponding oxides and a, b and c are constants which differ for each oxide. The values of a, b and c for silica soda, lime, magnesia and alumina are given in Table II.

Similar relations between the index of refraction and composition of the same glasses have been observed, but the values of a, b and c which are given in Table III for the partial index of refraction equations have not as yet been satisfactorily established.

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[1] More or less crystallized.

The accuracy of the results obtained by the method described in this paper justifies the prediction that tables can eventually be prepared from which it will be possible to determine the composition of a glass from its density and index of refraction. This will furnish a very satisfactory method for controlling the uniformity of composition of glasses without the delay incident to chemical analysis. Also, it will be possible to compute with much greater accuracy than is now possible the composition of a glass that will be required to give a specified index of refraction, which is a matter of extreme importance to the manufacturer of optical glass and to the designer of optical instruments.

NOTES ON THE OPERATION OF DIRECT FIRE TUNNEL KILNS[1]

By V. J. Roehm

ABSTRACT

The successful application of the direct fire car tunnel type kiln in firing of semi-vitreous chinaware is described. The bisque kiln firing to cone 9 one-half down is 332 feet 11 inches long, the placing height at middle of crown being 6 feet and the placing width 5 feet 1 inch. The glost kiln operating at cone 5 has the same placing height and width as the bisque but the length is 301 feet 1 inch long. The ware is placed in saggers as formerly. Natural gas is used as fuel and is supplied to kiln through Maxon Premix burners; an auxiliary fuel oil system can be used in case the gas is not available.

After a year's operation some of the important conclusions drawn are as follows:

1. The heat distribution is not ideal.
2. There is no appreciable difference in labor cost at this plant than in the older ones.
3. There is a considerable saving in fuel.
4. The sagger loss is much less than in the older type plants.
5. The direct fire tunnel kiln has proven successful from the commercial standpoint in manufacturing semi-vitreous china.

The two Harrop car tunnel direct fire kilns, one for bisque and the other for glost, were first producing ware at the new No. 6 plant of the Homer-Laughlin China Company, Newell, W. Va., the latter part of February, 1924. These kilns are firing only certain items of whiteware to meet a particular trade although they will fire satisfactorily all sizes and shapes of this type of ceramic ware.

The Equipment

Size of Kilns Both kilns are identical in every respect except in length and number of furnaces. The kilns are of the side vestibule type, the bisque being 332 feet 11 inches long from outside of vestibule to outside of vestibule and will accommodate 53 cars. The glost kiln is 301 feet 11 inches long from outside of vestibule to outside of vestibule, having accommodations for 48 cars. The cars are 6 feet 1 inch long, the placing width is 5 feet 1 inch and the placing height, excluding the height of setter blocks, being approximately 6 feet at the middle of the crown.

Pusher A hydraulic ram manufactured by the Oil Gear Co., Milwaukee, Wis., pushes the cars through the kiln at a constant speed. Under full load the pressure against the ram on the bisque is about 550 pounds while that of the glost varies from 340 to 380 pounds.

Temperature Control The temperatures under the cars and at 12 different positions along the length of the kiln, and at furnaces, Nos. 7 and 8 of the bisque, are gotten by means of 8 noble and 9 base metal thermocouples. On the glost 9 noble and 7 base metal couples

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[1] Recd. Feb. 14, 1925.

are employed to measure the temperatures under the cars, the last four furnaces, and at 11 different positions along the length of the kiln. The junction boxes are provided with temperature compensation coils. All terminals are located in a central control house situated between the discharge end of the bisque and the charging end of the glost kiln. The Leeds-Northrup potentiometer is used, each kiln having an indicating type which gives the temperature at any one couple and a three point recorder which records the three maximum crown temperatures. After eleven months of continuous service both types have given us complete satisfaction.

Furnaces Along the firing zone of the bisque kiln there are ten furnaces, five on each side. Each furnace is equipped with a Maxon Premix combination gas and oil burner. The glost kiln is equipped like the bisque with the exception, that there are eight furnaces, four on each side. When firing on a 90-minute schedule only eight furnaces are used on the bisque. Any faster schedule requires ten furnaces.

Fuel Oil System When oil is used for firing, the oil is first pumped from the storage tanks to the kiln shed level, at 20 pounds pressure. It is then pumped by means of a Viking pump, through a Lunkenheimer regulator, which keeps the pressure constant at about 45 pounds, then through a Powers heater, which pre-heats the oil to about 140°F after which it goes to the burners.

Gas Used So far the kilns have been fired almost continuously with natural gas, the pressure of the gas being kept within the limits of $4^1/_2$ and $4^3/_4$ ounces by means of an inside regulator for the glost and at about $4^1/_4$ ounces for the bisque.

Electric Power Required The electric current is 220 volts, 2 phase, 60 cycle alternating, and the electric power required for the bisque when firing on a 90-minute schedule with natural gas includes a 10 h. p. draft fan motor, a 10 h. p. pressure fan motor, eight $^1/_2$-h. p. burner motors and one $^3/_4$-h. p. pusher motor, a total of $24^3/_4$ h. p. The same amount of electric power is required for the glost kiln.

Operation of Bisque Kiln

Bisque Kiln Car Schedule The bisque kiln has been run on a 120, 115, 110, 105, 100, 95, 90, 85, 80, 75 and 70-minute schedules and good ware has been produced on all of them. The majority of the time the kiln has been run on a 90-minute schedule, the maximum temperature being 2060°F in crown. The time in the firing zone on a 90-minute schedule is 12 hours and 36 minutes. This brings cone 9 about $^3/_4$ down. Each bisque car has a capacity of 103

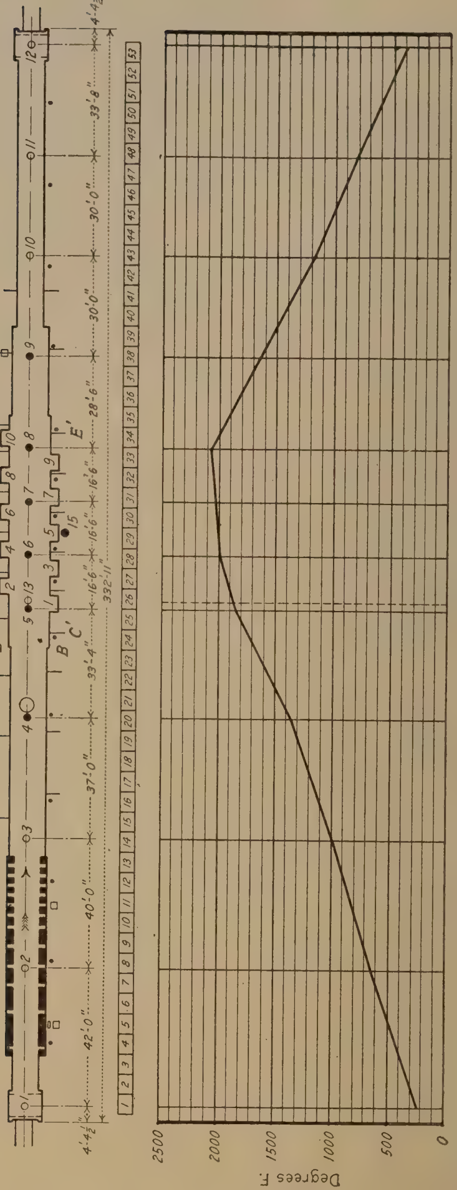

FIG. 1.—Bisque temperature record. 80-minute schedule at cone 9¾.

saggers or 300 dozens of ware. From this it appears that 16 cars are equal to an 18-foot periodic kiln.

Bisque Kiln Fuel Consumption On a 90-minute schedule the average gas consumption is 120,000 cu. ft. in 24 hours. An 18-foot periodic kiln requires on an average of 325,000 cu. ft. to fire off, so from these figures saving amounts to approximately 63%.

Draft Regulation Our experience has shown that the drafts should be so regulated that the neutral point (where the negative pressure balances the positive pressure) is between furnaces Nos. 1 and 2, and the draft gage at position "*C′*" (see Fig. 1), shows 0.040 inches of negative pressure. We have found that more uniform firing is obtained when there is a positive pressure down as far as No. 2 furnace.

Atmosphere Control The kiln gas has been drawn from the kiln at position *C′* (see Fig. 1) and the CO_2 and O_2 content determined. Below are given the tabulated results together with other data.

TABLE I

Date	Time	Per cent CO_2	Per cent O_2	Schedule Min.	Exhaust gas temp. °F	Gas consumption, cu. ft.
10/27/24	1:25 p.m.	5.1	12.3	90	410	136,500
10/28/24	9:10 a.m.	4.6	13.7	90	400	136,000
12/17/24	8:30 a.m.	5.8	14.2	90	490	131,000
12/19/24	10:25 a.m.	6.0	11.8	90	490	130,000
12/22/24	10:20 a.m.	5.4	13.0	100	480	113,000
12/23/24	9:15 a.m.	4.5	15.1	100	475	119,000
1/ 5/25	9:05 a.m.	4.2	13.6	100	450	117,700
1/ 6/25	8:45 a.m.	4.5	12.5	100	400	114,100
1/ 7/25	8:50 a.m.	4.8	12.1	90	400	115,600
1/ 8/25	10:30 a.m.	5.6	12.3	90	430	114,600
1/ 9/25	9:00 a.m.	5.0	11.4	90	400	113,800
1/12/25	9:00 a.m.	4.8	13.6	90	395	112,000

Av. CO_2 = 5.04% Av. O_2 = 13.0% Av. temp. 435°F Av. gas consumption, 121,000 cu. ft.

Temperature Control and Distribution Figures 4 and 5 show the temperature variations along the length of kiln obtained by means of an optical pyrometer focused upon the saggers at the middle part of car as to its height. Optical pyrometer readings were also taken at the top, middle and bottom of kiln at positions marked "*C*," "*C′*," "*E*" and "*E′*" (see Fig. 1).

The temperature variations are shown in Figs. 6 and 7. From the results one can see that the heat distribution is not perfect. This is in all probability due to the high velocity of the gas which pushes ahead at the top, while there is a stratum of cooler gases along the car tops. The mean velocity through the bisque kiln section at *C* (see Fig. 1) is 13.3 feet per second. But it is evident that in the more open positions it must be greater and in the tighter, slower.

The bisque kiln is much slower to respond when any marked change is made than the glost. The firemen are able to keep the temperatures more constant than that of the glost, but when they do get off it takes a much longer time to bring them back where they should be. The diminished fluctuations in the maximum crown temperatures of the bisque over those in the glost, I believe, can be attributed to the following reasons:

1. The cars travel through the kiln at a much slower rate.
2. The sagger settings are nearly uniform.
3. A smaller amount of air is required to cool the ware, therefore, the velocity of the gas is less.

z	y	x
8.81%	8.76%	9.17%
8.51%	8.26%	8.61%
7.79%	7.71%	8.04%
6.92%	7.13%	7.20%
6.97%	7.37%	7.34%
6.62%	6.42%	7.56%
6.19%	6.02%	7.14%
6.71%	7.23%	7.53%
6.77%	8.30%	8.46%

Absorption of ware from top to bottom in bungs *x*, *y* and *z*.

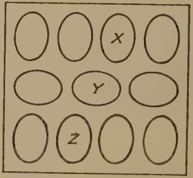

FIG. 2.—Top view of car showing bungs from which absorption trials are taken.

For the 90-minute bisque kiln schedule the time of preheating is 36 hours 47 minutes, the time within the firing zone 12 hours 36 minutes and the cooling time is 29 hours 15 minutes.

The effective heat distribution is best shown by the absorption of the ware from different parts of the car. In the illustration of Fig. 2, there is indicated the position of the different saggers and the absorption of ware contained in each. From this it appears that the heat effect in general is very satisfactory and much better than in the periodic kilns.

Operation of Glost Kiln

Capacity of Glost Kiln Each glost car has an average capacity of 75 saggers or 130 dozens ware. Figuring on the dozen basis eighteen cars are equal to a 16 ft. 6 in. periodic kiln. The kiln has been operated on a 60, 55, 50, 45 and 40-minute schedule according to the needed production. The schedule of 45 minutes has been followed the greater part of the time since the installation.

Fuel Consumption For this 45-minute schedule the average daily consumption of gas for 24 hours is 114,000 cu. ft. Figuring the average gas consumption of a 16 ft. 6 in. periodic glost kiln at 225,000 cu. ft., the fuel saving is approximately 71.0%.

Time Schedule The maximum temperature on a 45-minute schedule is 2000°F in the crown and at this tem-

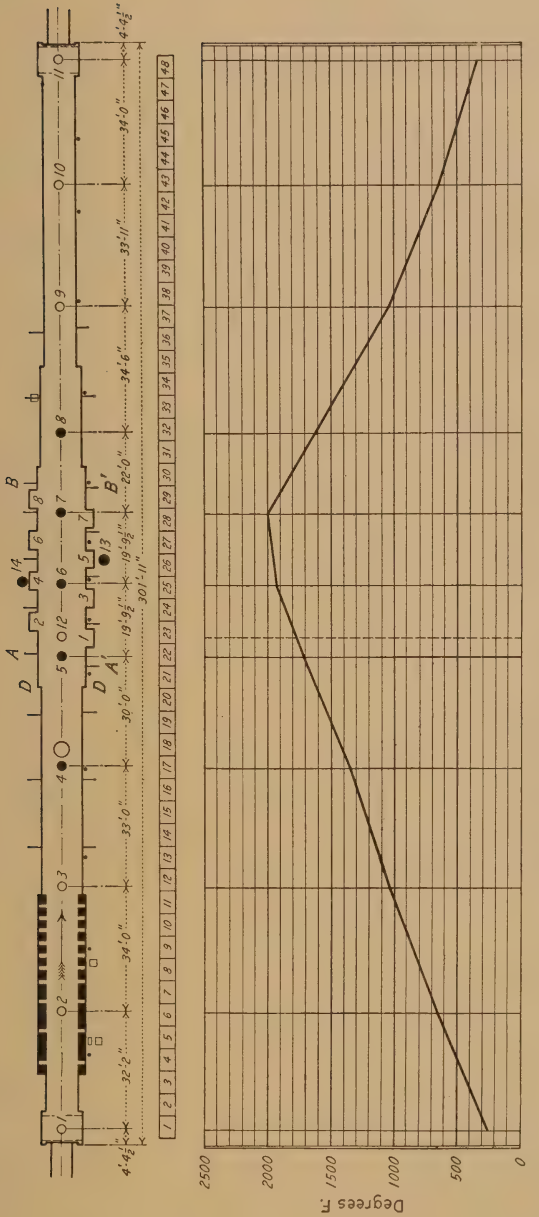

FIG. 3.—Glost temperature record. 45-minute schedule. Cone $5^3/_4$.

perature we get cone 5 about three-quarters down. It has been our experience that the 45-minute schedule is the fastest we can operate and still get a large percentage of first class ware. For several weeks the kiln was run on a 40-minute schedule the result being a noticeable amount of dull and easy ware. Another loss which became quite large was that of the saggers due to a more rapid heating and cooling. On a slow schedule the kiln is more flexible, the kiln firemen being able to keep more constant temperature and therefore a more uniform product results.

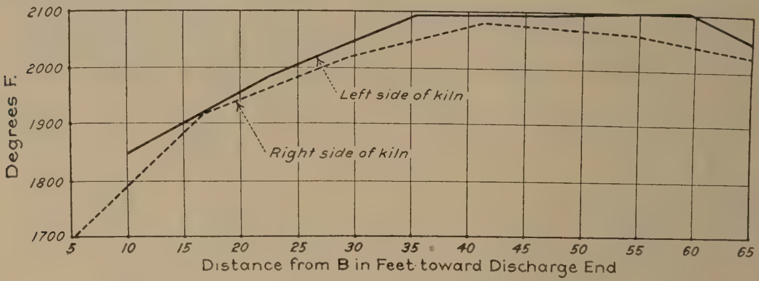

FIG. 4.—Bisque kiln. 90-minute schedule. (See Fig. 1.).

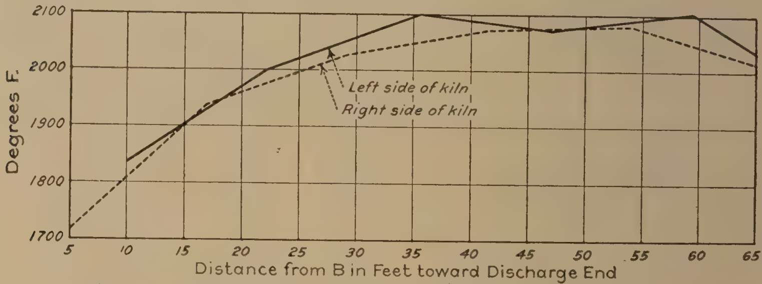

FIG. 5.—Bisque kiln. 80-minute schedule. (See Fig. 1.).

Atmosphere Control in Glost Kiln Some data was gathered as to the CO_2 and O_2 content of the kiln gases as they left the firing zone at position *A′* (see Fig. 3). Below are given some of the figures in tabulated form together with other data:

TABLE II

Date	Time	Per cent CO_2	Per cent O_2	Schedule Min.	Exhaust gas temp., °F	Gas consumption, Cu. ft.
5/17/24	8:40 a.m.	3.4	14.6	40	249	135,500
5/20/24	9:15 a.m.	3.6	14.4	40	261	146,000
5/21/24	12:00 p.m.	2.8	15.5	40	257	148,800
5/27/24	8:25 a.m.	4.1	12.7	40	253	138,000
5/30/24	7:40 a.m.	3.4	14.0	40	248	138,000
6/ 6/24	8:50 a.m.	2.3	16.5	45	244	134,000
6/10/24	8:45 a.m.	2.8	15.0	45	274	124,800
6/18/24	8:50 a.m.	2.8	14.8	45	271	118,000
6/26/24	1:15 p.m.	3.5	14.1	45	281	120,280

7/ 1/24	9:00 a.m.	3.2	14.4	55	302	119,300
7/ 2/24	9:05 a.m.	3.0	14.0	50	295	121,000
7/ 3/24	8:45 a.m.	3.2	11.8	50	267	120,000
7/ 6/24	8:30 a.m.	4.0	13.0	45	263	125,000

Av. CO_2 = 3.24% Av. O_2 = 14.06% Av. temp. 266°F Av. gas consumption, 122,000 cu. ft.

Draft Control in Glost Kiln

As to draft conditions we have found that the most satisfactory results are obtained when the neutral point is between furnaces 3 and 4, and the draft gage at A' (see Fig. 3) registers 0.055 inches negative draft. The temperatures of furnaces 5, 6, 7 and 8 are very important, and the firemen are warned to keep them at a minimum, and still hold the maximum crown temperatures. Invariably when the crown temperatures are up and the furnace temperature is 10°F above what it should be, we get some blistered and twisted ware in those saggers which pass close to the furnace mouths. This is also true when one has a slight flame in the combustion chamber. For this reason enough air is premixed with the gas till the flame disappears.

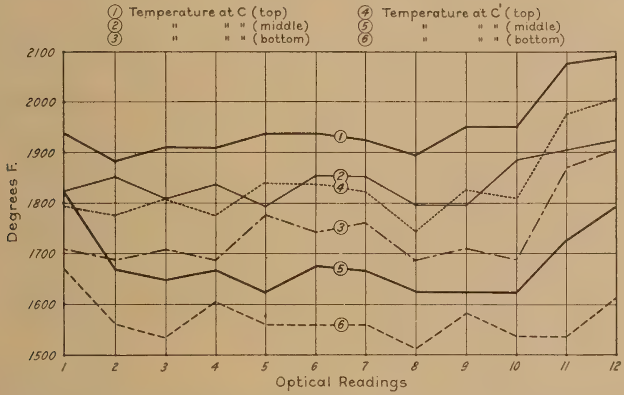

FIG. 6.—Temperature variations at C and C' (see Fig. 1) as found by optical pyrometer.

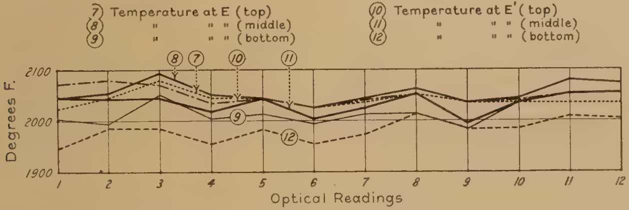

FIG. 7.—Temperature variations of bisque kiln at E and E' (see Fig. 1) as found by optical pyrometer.

Temperature Control in Glost Kiln Figures 8 and 9 show the results of optical pyrometer readings taken along the kiln representing the temperature of the outside sagger at the middle part of car as to its height. Optical pyrometer readings were also taken at the top, middle and bottom of kiln at points marked *A*, *A′*, *B* and *B′* (see Fig. 3). The results of these readings are shown on Figs. 10 and 11.

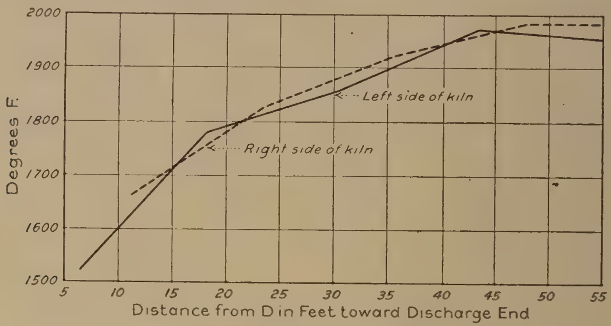

FIG. 8.—Glost kiln. 45-minute schedule. (See Fig. 3.)

From these curves it is seen that the heat distribution is not an ideal one and we believe that some of the streakiness is due to the high velocity of the gas in the kiln (about 18 ft. per second) which causes the gases to follow the line of least resistance.

The crown temperatures vary as much as 10°F at times, within 45 minutes. This is due in all probability to the variation in the sagger settings.

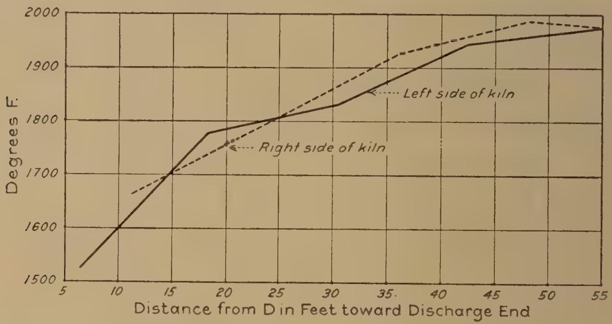

FIG. 9.—Glost kiln. 55-minute schedule. (See Fig. 3.)

In some cases the space between bungs is quite open and it does not extend very near to the crown of the kiln. In others the bungs are very tight, and are bunged to the maximum height. In the first case when a car so set comes into the hot zone the crown temperature begins to drop. On the other hand as long as there is a string of loose and low set cars a constant temperature can be maintained, but if a tight car with saggers bunged to the maximum height comes in between the loose set cars the crown temperatures immediately begin to rise. Endeavors have been made to keep the settings of the cars as uniform as possible, but since there are so many different sizes and shapes of saggers, it is really a big problem.

On a 45-minute schedule the time of preheating the glost ware is 16 hours 12 minutes, the time within the firing zone is 4 hours 54 minutes and the cooling time is 14 hours and 24 minutes.

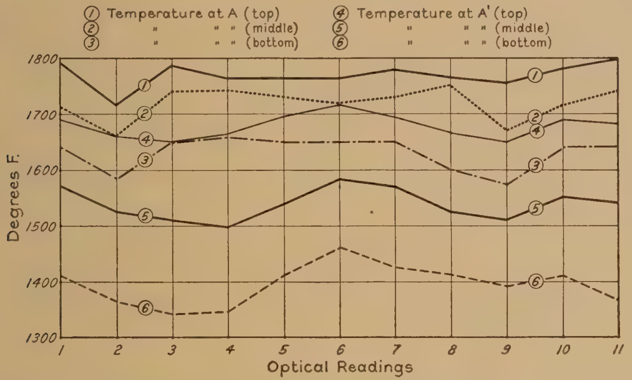

FIG. 10.—Temperature variations of glost kiln at *A* and *A′* (see Fig. 3) as found by optical pyrometer.

Economies

The two kilns are operated in three shifts of eight hours each. A crew is composed of a fireman and two helpers. The placing and drawing of the kilns are done on a day wage scale, the cost of placing being more than that of the older plants, while the drawing costs a little less. The average cost of both is a trifle higher than for the old style plants. The number of thirds produced in this plant are about 15% below that of the other plants. The sagger loss for both the bisque and glost kilns is approximately 35% lower than that of the older plants. In the eleven months of operation one wreck has occurred in the glost kiln, probably due to a faulty sagger; at this time the kiln was shut down for only six hours and the total time lost was not more than ten hours.

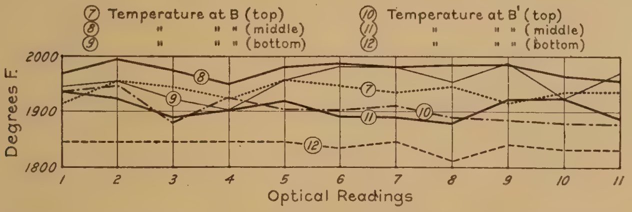

FIG. 11.—Temperature variations af glost kiln at *B* and *B′* (see Fig. 3) as found by optical pyrometer.

Summary

1. A 45-minute schedule on the glost is the fastest which is feasible without decreasing the quality of the ware. The greater the speed the more temperature variation will occur.
2. Minimum furnace temperatures on the glost are necessary to prevent excessive warping and blistering and they should approach the kiln crown temperatures as closely as possible.
3. A flame in the furnaces produces warped and blistered ware in the glost.
4. The faster the glost schedule the greater the sagger loss.
5. Under ordinary working conditions the heat distribution of both kilns is somewhat variable and is subject to improvement.
6. There is no appreciable difference in the labor cost at this plant than at the older ones.
7. There is a decided saving in fuel: approximately 67%.
8. The car temperatures should be maintained as high as possible without injuring the cars, so as to minimize the heat flow through the car platforms.
9. Further improvements should look toward the partial elimination of the flow of cooler air from the discharge end along the car platforms toward the firing zone. Likewise, the speeding ahead of the heated air under the crown both in the cooling and the heating-up section should be reduced as much as possible.
10. The regulation of the pusher speed is very important and it would be very desirable to work out an automatic regulator which would keep the speed reasonably constant.
11. The direct fire tunnel kilns have proven successful from the commercial standpoint, in firing of semi-vitreous table ware.

The writer wishes to thank A. V. Bleininger for his many helpful suggestions in preparing this paper and to J. P. Connor for getting much of the data.

The Homer-Laughlin China Co.
Newell, W. Va.

CERAMIC DRYING AND DRIERS[1]

With Special Reference to the Advantage of Controlled Temperature, Humidity and Air Movement

By A. E. Stacey, Jr.,[2] and H. B. Matzen[3]

Abstract

Construction for and principle of humidity drying.

Introduction

The art of successful ceramic drying is coming to be more and more appreciated as an "air processing" rather than a mere removal of moisture.

The law governing the rate of evaporation stated by Carrier, Lewis, Himus, Hinckley, Fisher and others, is: "The rate of evaporation varies with the velocity of the air in contact with the wet surfaces and also is dependent on the difference in the temperature between the wet and dry bulb temperatures of the air." This last is known as the wet bulb depression. This is approximately constant for any relative humidity at different dry bulb temperatures.

As it is essential to control the rate of drying, a drier, to be entirely successful, must provide a uniform brisk circulation of air over all parts of the material, and be so designed that the temperature and relative humidity are controllable, either manually or automatically.

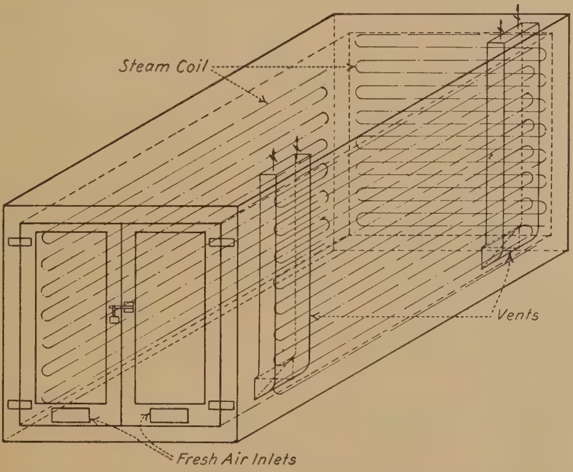

Fig. 1.—Early type of drier using gravity air circulation.

Types of Driers and Air Circulation

Driers are divided into two general types, as to method of air circulation, one depending on gravity and the other on mechanical means.

Figure 1 illustrates one of the earlier examples of driers, which depend on gravity for air circulation. The air first comes into contact with the hot heating surfaces and then with the material. As it passes through the material, evaporating moisture, it is cooled, falls to the floor, and again passes through the heating coils. The resulting circulating is neither positive nor uniform and results in great unevenness in temperature and drying rate. As evaporation would entirely cease if the air in the drier were continuously recirculated until it becomes saturated with moisture, vents and fresh air openings are provided. These are arranged with regulating dampers which can be manipulated so as to give an approximate control of the relative humidity through the introduction of dry, fresh air. However, due to lack of positive circulation, rapid even drying cannot be obtained.

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[1] Presented at the Annual Meeting, American Ceramic Society, February, 1925. (Heavy Clay Products Division.)

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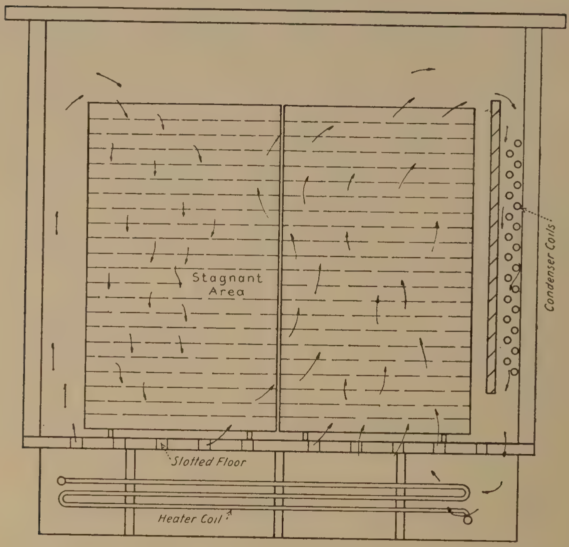

FIG. 2.—Drier using slotted floor and gravity circulation.

Figure 2 is a development from the first drier, using a slotted floor with the heating surfaces grouped underneath. The circulation of the air is by gravity. Later, condenser coils were added. Cold water was circulated through the coils in sufficient quantity to condense from the air, moisture evaporated from the material. The condenser coils also assisted in accelerating the movement of the air through the drier. Very uneven drying occurred in this type, due to no method of positive air circulation.

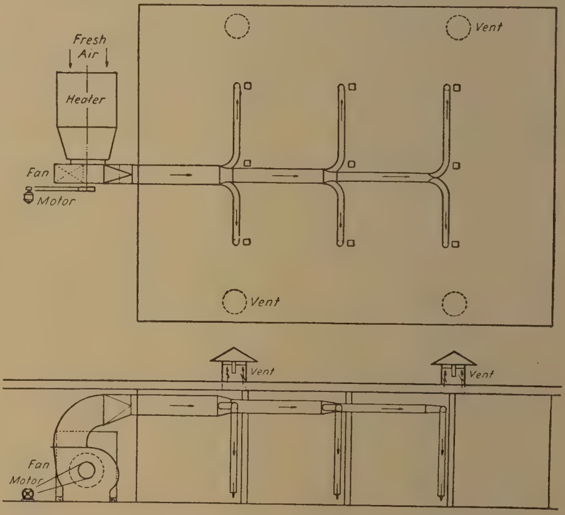

FIG. 3.—Early type of drier using forced circulation of air.

There are many variations of the

gravity type of drier and it is possible, with careful operation, to obtain successful results, but at a very *slow* rate.

The first driers with positive mechanical circulation were almost uniformly a failure. This was due largely to the method used in air introduction and utter lack of any provision for humidity control.

Figure 3 shows one of the earlier arrangements of apparatus and air distribution. It will be noted that only fresh, dry air passed through the apparatus, which was discharged through drop pipes against the floor and then passed up through the material and escaped through the vents in the ceiling.

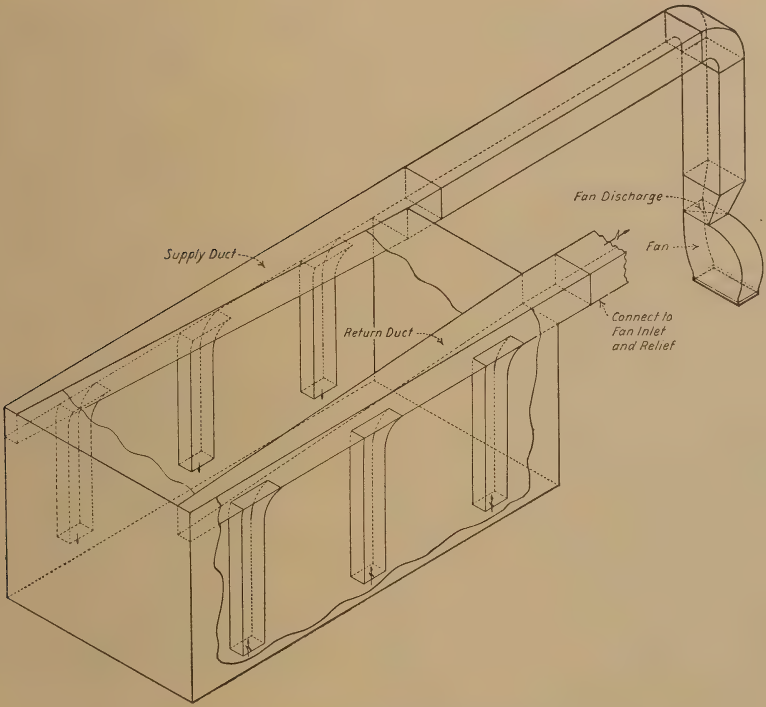

FIG. 4.—Drier using forced recirculation of air.

As a result of this exposure to extremely dry air, general injury to the ware often occurred. This type of drier was also very uneconomical as all the air used had to be heated from atmospheric temperature to the temperature of the drier, and then exhausted after one passage over the material. Unfortunately, it is impossible, with this method, as shown, to produce a rapid, even flow of air through the material. However, such a method of air circulation, if properly designed, might be made to give rapid, even distribution.

Another type of circulation with a fan, is shown in Fig. 4. In this case, the air is introduced through outlets near the floor, along one side of the room, and discharged by the same method from the opposite side. The air passed through the room unevenly, there being a zone of high velocity at the center, and very low velocity near the upper part of the room, along either side.

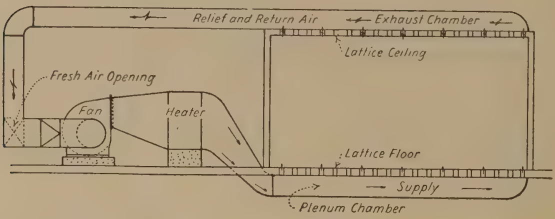

FIG. 5.—Mechanical circulation of air through perforated floor and ceiling.

Figure 5 illustrates a system of air circulation by mechanical means with lattice floors and ceiling. The success of this arrangement depends entirely on the proper ratio of air volume to openings through the floor. The resistance of the floor to flow of air must be greater than the pressure corresponding to the velocity of the air through the chamber underneath. In this way a uniform flow of air will result over the full area. With care in operation, this system should be able to give good results. This type of circulation is varied by using solid floors and perforated side walls.

Figure 6 is an example of mechanical circulation using the disc type of fan in place of the centrifugal housed fan. In this figure, the air is drawn through the material, although this may be varied by reversing the direction of the air flow. In this case there is a direct blast of air on the material with the necessary unevenness of drying rate. The mechanical efficiency of

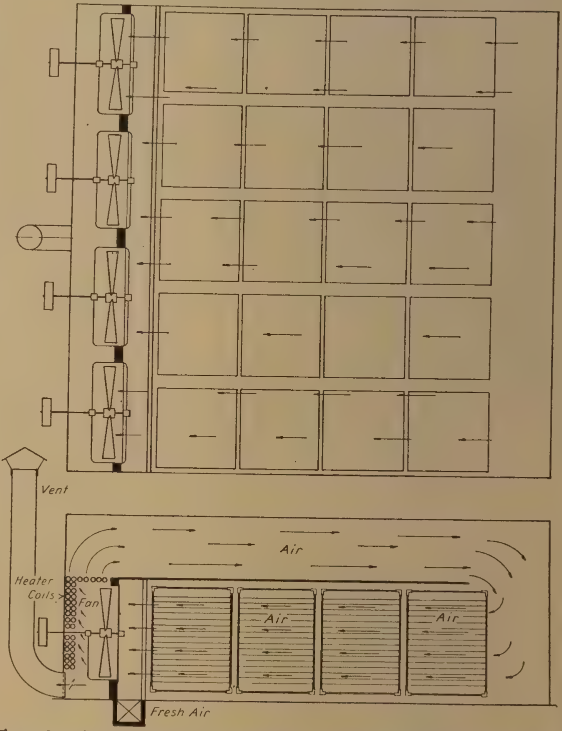

FIG. 6.—Mechanical circulation of air by means of disc fans.

the propeller type of fan is much lower than that of other types of fans, which makes the installation inefficient from the power standpoint, except for the fact that low pressures are usually required.

One of the most recent improvements in the method of air circulation and distribution is the ejector system, which is illustrated in Fig. 7. This system employs the highly efficient, housed, centrifugal discharge fan, discharging the air through nozzles at high velocity. Due to the high velocity of this air, a secondary current, three to five times the original volume, is set in circulation. The ejector nozzles are placed along one side of the room, near the ceiling, discharging the air over the material. This air mixes thoroughly with the larger volume of room air as it passes across the top of the material. As it reaches the far side of the room, it is deflected downward along the wall from where it passes backward, horizontally through the material, in an opposite direction from the discharge of the nozzles. Due to the resistance to the flow of air offered by the material, a slight pressure is built up on the farther side of the room, thus equalizing the flow through the material and maintaining a strong uniformly distributed current over the drying surfaces.

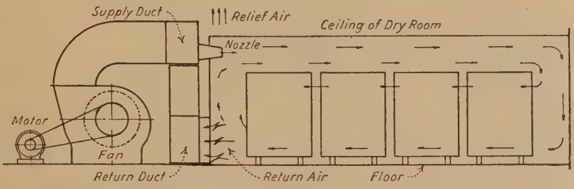

FIG. 7.—The ejector system of air circulation.

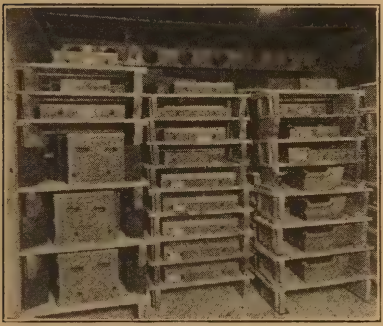

FIG. 8.—Ejector room, drying terra cotta on pallets.

The ejector system is a development of great importance because it makes possible the circulation, within the drier, of much larger volumes of air than are possible otherwise. This is so, because an apparatus which will condition and propel a given volume of air can, by means of this system, circulate within the drier, three to five times as much air as introduced.

Several methods of arrangement of material are used with this system. The material may be placed on pallets, as illustrated in Fig. 8. The pallets are moved in and out of the drier on lift trucks.

Figure 9 shows one method of handling sanitary ware on stillage. These racks are moved on lift trucks, which allows loading at the point of reworking.

Figure 10 illustrates a method of handling by means of an overhead trolley system. In this case, the stillage is reloaded at the rework bench.

It is then moved into the drier and after drying, to the sanding and inspection departments.

Temperature and Humidity Control

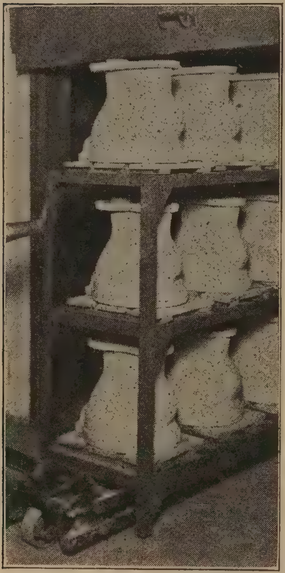

Fig. 9.—Ejector room, drying sanitary ware on racks.

The foregoing has been a description largely of methods of air circulation, which is one of the prime necessities of successful drying. However, it is as important to be able to control the drying conditions, as well as to have proper air circulation. Since the rate of drying depends not only on the air velocity, but also on the difference between the wet bulb temperature and the dry bulb temperature, the rate of evaporation must not be greater than the rate of moisture diffusion through the material. This may be stated in another way, as follows:

That the evaporation from the surface of the body must not be in excess of the movement of the moisture from the interior to the surface. As the rate of diffusion is a function of the temperature, it is necessary for rapid, successful drying, to increase the temperature of the material to as high a temperature as the piece will stand without injury. The temperature of the material, so long as it remains above the "particle saturation point," will be approximately at the wet bulb temperature of the air; so, by controlling the wet bulb temperature, it is a simple matter to control the temperature of the material, or rate of diffusion. Under conditions of constant air movement, it is necessary to control the wet and dry bulb temperatures of the air, in order to control the rate of successful drying.

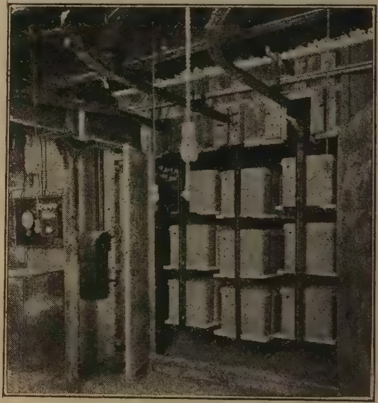

Fig. 10.—Ejector room, drying sanitary ware on racks moved by overhead trolley system.

Instruments for Automatic Control

Highly developed instruments for the control of conditions, as cited above, are now in general use. Such instruments are affected, either by the wet bulb and the dry bulb temperatures directly, or by the dry bulb temperature and the relative humidity. The first condition requires two thermostats, one exposed to the dry bulb temperature and the other wetted and affected by the wet bulb temperature. The second condition requires a dry bulb thermostat and a hygrostat with a hygroscopic member, affected by the relative humidity of the air. This is permissible, inasmuch as the difference between the wet bulb and dry bulb temperature remains approximately constant, for any given relative humidity. This difference increases slightly with an increase of temperature, so that a slight drying effect may take place during the last part of the heating-up period. The following examples are given as typical of methods of automatic wet bulb and dry bulb controls:

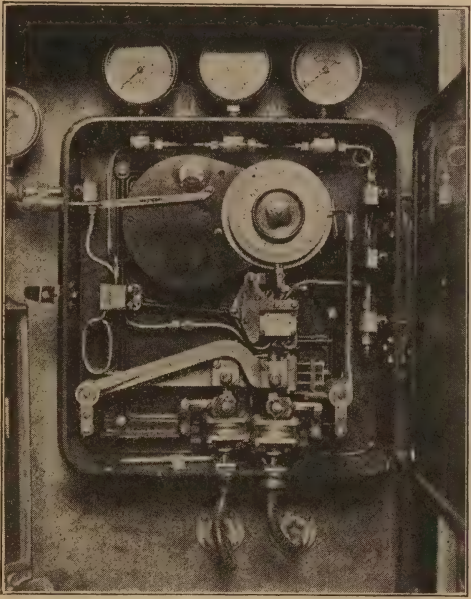

FIG. 11.—The Thermotyme automatic control for wet and dry bulb temperatures.

Figure 11 illustrates the Thermotyme wet and dry bulb control. This instrument embodies, in one case, two variable thermostats, one controlling the dry bulb temperature by means of admission of steam to the heaters, and the other, the wet bulb temperature, through a steam spray or other humidifying device. The control setting of these thermostats is continuously changed, according to a predetermined schedule. This is accomplished by means of cams "*A*" and "*B*," which are driven by a clock. The action of the cams changes the setting of the thermostats automatically in a more accurate manner than can be done by hand, and are independent of the human element. As the temperature and wet bulb depression will be the same during every run, the rate of drying will be the same every day, irrespective of loadings of outside atmospheric conditions. However, the instrument is not restricted to one drying schedule by the shape of the cams. Should it be desirable to raise or lower the temperature plane of the entire schedule, this can be done by a simple adjustment under

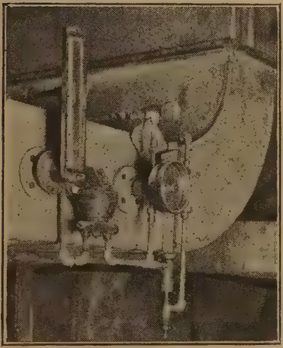

FIG. 12.—Control for temperature and relative humidity.

the valve block. If it is possible to reduce the duration of the heating-up period, this can be accomplished by an adjustment at the side of the instrument. By changing the speed of the clocktrain, the entire schedule may be shortened or lengthened. So, the drying of many pieces of different characteristics can be carried on under schedules best suited for their requirements.

Another type of ceramic drier control is illustrated by Fig. 12. This is of particular value in the drying of materials which are not sensitive to slight changes in the length of schedule. The action of this control is to maintain constant relative humidity by a hygrostat and humidifying device throughout the heating-up period, at the end of which the hygrostat is automatically cut out of the system by a thermostat, and the drying proceeds under dry bulb control alone. In this case, the humidity is gradually decreased by infiltration of the outside air, until the end of the drying period.

Drying Schedules

As the maximum rate of drying, without injury, depends on the characteristics of the mix and the shape of the piece, it is necessary to determine the proper drying schedule to fit each individual case. However, experience has shown that in general, different types of material will have the same characteristic schedules. These may be modified somewhat, due to different clays, etc.

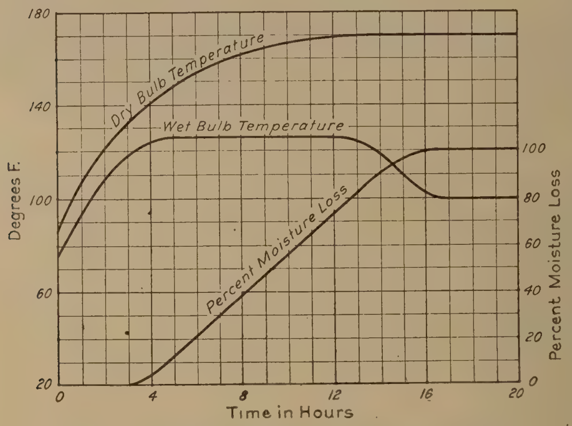

Fig. 13.—Typical terra cotta drying schedule.

Figure 13 illustrates a general schedule of drying for terra cotta, for pieces under one hundred pounds. This schedule has the characteristic heating-up period, which extends over the first three hours. In this case, the temperature increase is more rapid than would be possible with mixes of more delicate ware. The conditions during the drying period show a rapid increase in dry bulb temperature, with a decreasing wet bulb, which is most favorable for a rapid rate of evaporation.

As the final amount of moisture left in the material is dependent upon the difference between the wet bulb and dry bulb temperatures, it is necessary to reduce the wet bulb to a low point at the end of the drying period.

The amount of moisture which may safely be left in a piece, at the end of the drying period, depends on the rate of firing in the kiln. If slow, 4% to 6% will not cause any damage, but if rapid, 2% would seem the point to be the maximum.

In general, the rate of change in temperature of the piece itself, and the rate of evaporation from the surfaces, are the determining factors in the arrangement of a drying schedule. As the variation of temperatures in the piece depend on air circulation, as well as upon temperature and the relative humidity, it will be seen that schedules will vary for different types of driers, for drying the same material.

Conclusion

The benefits to be derived by modern drying equipment employing reliable control of temperature and humidity and air movement, have been well demonstrated by several successful installations in large plants of this country. Although there is much that can yet be accomplished in drying practice, and this must be done by the proper coöperation of the progressive manufacturers and those who are specialists in the air conditioning field, the early experimental stages have been passed.

Installations of the nature described are successfully drying sanitary ware, whiteware, tile, terra cotta, refractories, glass pots, electrical porcelains and other of the finer grades of ceramic products.

The improvement in drying practice accomplished by modern systems may be stated in terms of definite profit to the manufacturer; drying breakage is reduced to a minimum; the time of drying is standardized; the amount of unfinished ware in stock is cut to a minimum and the floor space for drying is reduced to a small percentage of that formerly necessary.

CARRIER ENGINEERING CO.
NEWARK, N. J.

THE OXIDATION OF CERAMIC WARES DURING FIRING.[1] VI. A LABORATORY STUDY OF THE EFFECT OF VARYING THE RATE OF GAS FLOW AND OF HEATING ON THE DECOMPOSITION OF PYRITE IN CLAY

By Frederick G. Jackson[2]

ABSTRACT

This investigation shows that varying the rate of heating has little effect on the evolution of sulphur as gases from pyrite. Varying the rate of atmospheric flow, however, exerts a very marked effect. With a rapidly moving atmosphere the sulphur is 90% removed below 510°C (950°F), even when heated rapidly. Explanations are made and the application of the results to industry is pointed out.

Hitherto in the laboratory study of the evolution of sulphur from clays,[3] the rate of gas flow and the heating schedule have been held constant and the effects of different atmospheres and of different impurities in the clay studied. In the present investigation, a constant atmosphere (100% excess air) and a constant impurity, pyrite, a very common one in commercial clays, are used. The rate of gas flow and the rate of heating are varied.

The effect of varying these conditions is studied because from theoretical considerations, it was thought that they must have a very great bearing on the chemical reactions which take place in the firing of pyrite bearing clays.

Method of Procedure

The general methods used in preceding investigations were followed exactly. A number of bars were made up, using for each one 60 grams of the same secondary kaolin that was used before and $1^1/_2$ grams of pyrite, ground to pass 60-mesh. These bars were dried at 110°C. For each test a bar was heated in the electric resistance furnace, an atmosphere of known composition was passed through the combustion tube at a carefully regulated speed, and the sulphur in the exit gases was absorbed and analyzed. This apparatus has already been fully described and a photograph shown.[4] In the present investigation an entering atmosphere of uniform composition was used in all tests. It was approximately equivalent to 100% excess air in a coal fired kiln, and was made up as follows: 10% CO_2, 40% N_2, 50% air. This atmosphere was prepared in 20-liter bottles. It was applied at three different rates in the different tests, namely, 5, 10 and 20 liters per hour. In previous similar studies[5] the gas was passed at a rate of approximately 10 liters per hour. The importance of carefully controlling this rate was not at first fully recognized. In consequence, some of the results obtained were somewhat difficult to explain.

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[1] Published by permission of the Director, U. S. Bureau of Mines, Department of the Interior.

[2] Associate Chemist, Ceramic Experiment Station, Bureau of Mines.

[3] *Jour. Amer. Ceram. Soc.*, 7 [4], 223; [5], 382 (1924).

[4] *Loc. cit.*

[5] *Loc. cit.*

These particular rates of gas flow were selected after a study of results obtained in tests on commercial kilns.[1] In the third industrial study described, the rate of gas flow through the kiln during the first part of the sulphur evolution averaged 14 liters of cool gas for every 60 grams of charge. The amount of surface exposed per unit weight was five times as great in this work as in a commercial kiln.

The heating schedule used in previous studies was also maintained in this work. It had been derived from the first industrial study by dividing the hour factor of the schedule by ten, after attaining 425°C in the first hour. In the present investigation the temperatures attained in equal intervals of time were always the same as in the previous work. The length of these intervals was varied in the different series of tests. Thus in one series, two hours were allowed to attain each temperature of the schedule, in another series one hour, and in a third series one-half hour. The schedules were as follows:

TABLE I

HEATING SCHEDULE

Slow heating (hours)	Medium heating (hours)	Rapid heating (hours)	Temp., deg. C
2	1	½	425
4	2	1	445
6	3	1½	480
8	4	2	510
10	5	2½	560
12	6	3	615
14	7	3½	665
16	8	4	775

The absorbers for SO_3 and SO_2 were changed at the end of each interval and the amounts of gases absorbed were determined. A test was made with each rate of atmosphere passing at each rate of heating. This made nine tests.

Results

The results of these nine tests are recalculated as the percentage of the total amount of sulphur that was given off during each interval. This was done uniformly with results in previous work.

These results may give a clearer impression if presented graphically. The method used in the previous work is used here and cumulative results are plotted. In each figure, any point on the lower curve represents the

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[1] *Jour. Amer. Ceram. Soc.*, **7** [8], 634 (1924).

TABLE II

PER CENT OF SULPHUR EVOLVED. FIVE LITERS OF GAS PASSING PER HOUR

Temp., deg. C	Slow heat (16 hours)		Medium heat (8 hours)		Rapid heat (4 hours)	
	as SO_3	as SO_2	as SO_3	as SO_2	as SO_3	as SO_2
425	0.15	3.25	0.20	3.12	0.19	3.77
445	1.62	24.32	2.30	40.40	1.35	26.79
480	0.26	13.18	0.18	6.78	0.17	2.49
510	.29	0	0	.08	.09	0.25
560	.48	10.75	0	.07	.18	.28
615	.14	.38	0	.10	.20	1.69
665	.15	.37	0	.10	.08	0
775	.38	40	0	.05	.02	.55
Totals	3.47	52.65	2.68	50.70	2.28	35.82
Total per cent sulphur evolved in test	56.12		53.38		38.10	

TABLE III

TEN LITERS OF GAS PASSING PER HOUR

Temp., deg. C	Slow heat (16 hours)		Medium heat (8 hours)		Rapid heat (4 hours)	
	as SO_3	as SO_2	as SO_3	as SO_2	as SO_3	as SO_2
425	0.94	33.90	0.25	1.04	0.11	2.16
445	2.82	41.35	2.02	36.34	1.56	27.36
480	2.32	4.95	3.20	40.37	1.42	30.68
510	0.22	.05	0.36	0.25	0.11	1.22
560	.42	.20	.10	.05	.98	14.13
615	1.13	.40	.21	.15	.19	1.45
665	.39	.30	.08	.20	.06	0.15
775	.78	0	.22	.15	.16	0
Totals	9.02	81.15	6.44	78.55	4.59	77.15
Total per cent of sulphur evolved in test	90.17		84.99		81.74	

TABLE IV

TWENTY LITERS OF GAS PASSING PER HOUR

Temp., deg. C	Slow heat (16 hours)		Medium heat (8 hours)		Rapid heat (4 hours)	
	as SO_3	as SO_2	as SO_3	as SO_2	as SO_3	as SO_2
425	1.98	35.48	0.80	31.15	0.41	11.95
445	8.61	46.87	2.28	51.75	1.06	45.20
480	1.11	0.10	2.72	1.60	0.71	19.30
510	0.89	0	0.65	0	1.47	9.25
560	.45	.10	.27	.10	0.60	0.45
615	.67	0	.36	.15	.39	.30
665	.48	.05	.24	.10	.41	.20
775	0	0	.80	.30	.70	.60
Totals	14.19	82.60	8.12	85.15	5.75	87.25
Total per cent of sulphur evolved in test	96.79		93.27		93.00	

precentage of total sulphur evolved up to that temperature as SO_3 and the upper curve the percentage of total sulphur evolved in all forms. The difference between the two curves represents sulphur as SO_2.

Figure 1 shows the three tests when the gas was passed slowly, five liters per hour. Figure 2, when the gas was at a medium speed—ten liters per hour, and Fig. 3 when the rapid rate of twenty liters per hour was used.

The yields of sulphur in each case are summarized in the following table:

TABLE V

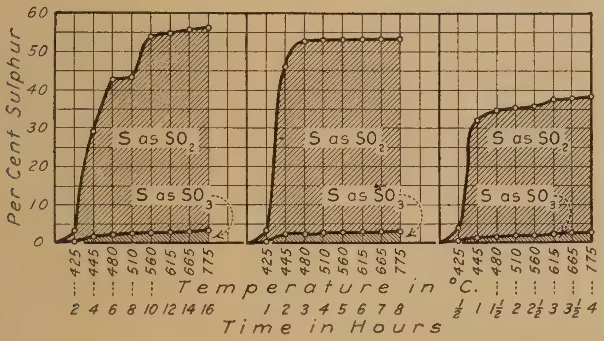
TOTAL PERCENTAGE OF SULPHUR YIELDED UNDER VARYING CONDITIONS

	Slow heat	Medium heat	Rapid heat
Slow gas	56.12	53.38	38.10
Medium gas	90.17	84.99	81.74
Fast gas	96.79	93.27	93.00

Discussion of Results

These results bring out very strikingly the object of the investigation. *Changing the rate of gas flow has a much greater effect on the yield of sulphur at low temperatures than changing the rate of heating.* A mathematical formula might be derived for this. It would, however, probably be of little value because in actual practice, there are too many variables involved.

Calculation shows that twenty liters of the gas mixture used contains 1.20 grams of oxygen. This will burn an equal weight of sulphur to SO_2.



Slow Gas
Slow Heat

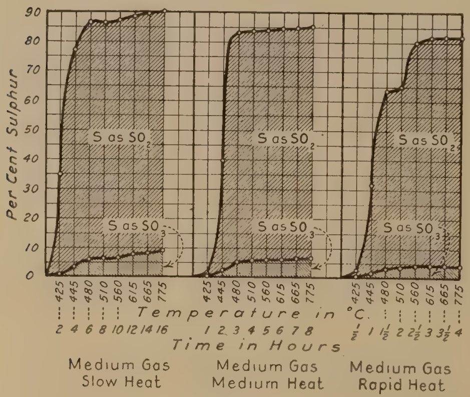
Slow Gas
Medium Heat

Slow Gas
Rapid Heat

FIG. 1.

There were 1.5 grams of FeS_2 put into each clay bar. This amount contains 0.80 gram of sulphur. When FeS_2 first decomposes to Fe_7S_8 and S, three-sevenths of the sulphur is evolved. This weighs 0.343 gram. The oxygen to burn this is furnished by 5.7 liters of gas. To oxidize all the sulphur in a bar requires 14 liters of gas. The oxidation of the iron to Fe_2O_3 must also be considered. This requires 0.30 gram of oxygen or five liters of gas. In all, nineteen liters of gas are required to furnish the necessary oxygen for the reaction.

To apply these figures, let us consider first the cases where gas was passing relatively more rapidly than the heat is being increased. In the extreme case (rapid gas—slow heat) 40 liters of gas were passed for every temperature interval. When the pyrite started to oxidize the temperature intervals were 20°C. Therefore enough oxygen was furnished, after the reaction began, to complete the oxidation before the temperature had increased by 10°C. The yield was 92.94% of the sulphur during the first two intervals. The remaining 7.06% of sulphur was evidently converted to $Fe_2(SO_4)_3$ almost completely since the gas evolved during the rest of the test was 3.60% SO_3 and 0.25% SO_2.[1]



Medium Gas Slow Heat

Medium Gas Medium Heat

Medium Gas Rapid Heat

FIG. 2.

In the next group of tests, rapid gas—medium heat and medium gas—slow heat, 20 liters of gas were passed for each temperature interval attained, and so there was enough oxygen furnished to complete the oxidation before the temperature had increased by 20°. Yields were high, 93.27% and 90.17%, the more rapidly moving atmosphere giving the better yield. In both these cases, after the third interval, the bulk of the gas evolved was as SO_3, indicating that the remaining sulphur had been oxidized, probably to $Fe_2(SO_4)_3$ which in turn was decomposing at the higher temperature.

In the three cases where rate of gas flow and of heating were relatively the same, sufficient oxygen to complete the oxidation of the pyrite was furnished every two temperature intervals, or while the pyrite was being heated 45°. Yields were 93.00%, 84.99% and 56.12% depending on the rate of gas flow. When the gas was moving rapidly and sweeping away the products of combustion as rapidly as they were formed, the yield was high. But if the SO_2 formed could lie in contact with oxidizing iron, it was absorbed by it. In the fourth paper of this series it was shown[2] that the tendency to form ferric sulphate from Fe_2O_3 and $SO_2 + SO_3$

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[1] In the second paper of this series (*Jour. Amer. Ceram. Soc.*, 7 [5], 384 (1924)) it was found that in 100% excess air ferric sulphate was practically stable until heated to 560°C and then decomposed evolving more SO_3 than SO_2.

[2] *Jour. Amer. Ceram. Soc.*, 7 [7], 532 (1924).

doubled between 350° and 415°. It was shown that some complex, stable up to higher temperatures, and referred to as "ferrous sulpho-silicate" was readily formed at these temperatures. In the test with slow gas and slow heat, it is evident that both of these compounds are formed to a considerable extent. There is an evolution of 11.23% of sulphur during the fifth interval, indicating ferric sulphate, but 43.88% of the sulphur was not evolved by the end of the test, which would point to the formation of a more stable complex.

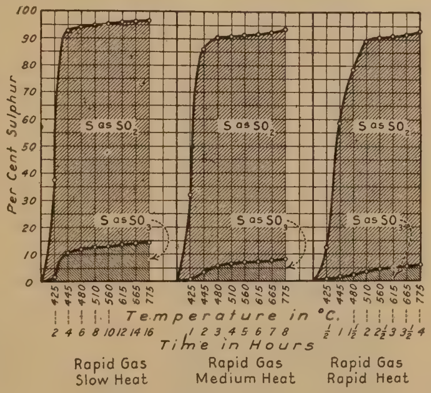
With medium gas—rapid heat we find the same kink at the same place in the curve, indicating the presence of ferric sulphate. In this test, as with slow gas—medium heat, sufficient oxygen for the oxidation was furnished every four temperature intervals. Even the 5.7 liters of gas needed to oxidize the first part of the sulphur, by the reactions:

$$7\ FeS_2 = Fe_7S_8 + 6\ S$$
$$6\ S + 6O_2 = 6\ SO_2$$

was not supplied for more than an hour. In consequence, when the first reaction took place rapidly of its own accord, the second continued until the oxygen supply was exhausted. The remaining sulphur then was free in elemental form. It was washed over, in an atmosphere of N_2 and SO_2, by the water of constitution of kaolin which is given off at about this temperature. This elemental sulphur could readily be seen in the absorbers.

It is evident that almost all of the remaining sulphur is combined as the more stable complex, since, after the third interval there is practically no sulphur evolved.

With slow gas—rapid heat, during the entire test there was only just enough oxygen passed to perform all the oxidation required. The main yield of the sulphur came in elemental form during the second interval. After that the Fe_7S_8 remaining could oxidize only slowly in insufficient oxygen and at high temperature. The tendency would therefore be to form the more stable complex.



Rapid Gas
Slow Heat

Rapid Gas
Medium Heat

Rapid Gas
Rapid Heat

FIG. 3.

Conclusions

Pyrite may be readily and almost completely decomposed at low temperature if sufficient oxygen is provided. The oxygen need not be concentrated, as was the case in some previous laboratory tests, but need be only 10% of the atmosphere. This atmosphere, however, must be moving rapidly, to give good yields. Thus enough oxygen is provided and the sulphur gases are swept away before the temperature increases greatly. In experiments where volume of gas per temperature interval is the same, the more rapidly moving gas gives the greater evolution of sulphur. If the sulphur gases are not removed rapidly, they recombine with active materials in the ware to form compounds which are decomposed only at higher temperatures. If such compounds are formed in large amounts, their decomposition may injure the ware.

RECUPERATOR OIL SMELTER[1]

By Robert MacDougall

ABSTRACT

A recuperator was built at small cost to serve a unit of two oil-fired smelters. These smelters have shown a fuel saving of $2500.00 per year over cost of coal for smelters formerly used, besides saving the labor of one man. An improved product results from better furnace control possible with oil fuel and preheated air for combustion.

A year ago our producer coal smelters were in need of replacement. After considerable study we decided to design and build four oil smelting furnaces. These furnaces were designed and built, two furnaces to a unit, a common stack serving both. Two of these furnaces were built so that their operation could be studied before building the additional furnaces.

The efficiency of the average smelter is very low, perhaps as low as any commercial furnace of any type. In designing these oil furnaces we set out with the idea of increasing the efficiency, and at the same time get maximum heat control.

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb., 1925. (Enamel Division.)

These furnaces are the common type smelter, each having a single pot or tank made up of 20–24 inches by 12 inches by 6 inches Laclede-Christy No. 30 mix flux blocks. A common stack is located in the five-foot space between and near the back of these furnaces. The burner and flue openings are on the same end of each furnace, about 3 feet apart. A 6-inch square opening is provided in the center of the arch for charging the mix and a 10-inch square sliding door is placed in the front above the spout and pot for stirring the smelt. The total combustion volume above the pot is 50 cubic feet. The flue area is 90 square inches, and the stack diameter is 18 inches. The stack is divided to 18 inches above the flues.

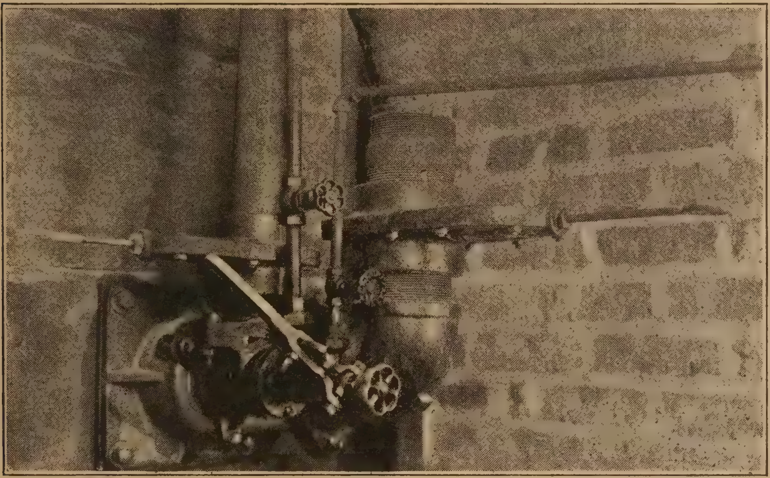
The efficiency of an ordinary smelter is low, due principally to: (1) high temperature of flue gases, (2) radiation loss, (3) oxidizing atmosphere maintained.

The greatest opportunity to save fuel is utilization of a portion of the heat in the flue gases, as this loss is usually 70% or more in a furnace of this type. The radiation loss may run around 15%. Twenty per cent excess air in the furnace will account for a loss of perhaps 8%. If 30% of the radiation loss could be saved through insulation, only a 5% increase in efficiency would result. However, if 30% could be saved from flue gases an overall saving of 23% would be effected. There has always been a question of the practicability of insulation on high temperature furnaces.

On glass tanks, regeneration is common practice, but this is impractical for furnaces intermittently operated. The practicability of a metallic recuperator, using 2600°F flue gas with the other corrosive gases from the smelt is perhaps questionable. We solved the recuperator problem in a very simple manner.

The stack is 10-gage steel, 27-inch diameter by 24 inches high, lined with Mount Savage arch brick, leaving a flue 18 inches in diameter. The stack was made in two lengths bolted together; the lower part 14 feet long being arranged for a recuperator by the addition of an air-tight outer steel casing 30 inches in diameter with a 12-inch air inlet introduced at the top off center. The outlet is at the bottom and off center, as at the top, causing the air to swirl around the stack in a narrow stream.

The burners used are special No. 4 Hagan Burners with a capacity of 12 gallons of oil per hour. One burner is used on each furnace. The burner has a $2^1/_2$-inch atomizing air connection and a 4-inch combustion air connection. The atomizing air at $1^1/_2$ pounds pressure is preheated to 200°F in a pipe coil in the brickwork of the arch. The combustion air is introduced at a pressure of about $^1/_2$ ounce and is preheated in the stack to 500°F. An asbestos shutter is provided to slide in front of burner nozzle when burners are shut off. It is not necessary, however, to use this shutter when the burner is shut off for the short time during charging.



A comparison of the fuel cost of operating the old and new furnaces is interesting.

Each of the coal producer furnaces had two pots; the front pot was used to smelt white, and the back pot first coat enamel. The output of each furnace per 24 hours was as follows:

11 charges of 470 lbs. white or	5170 lbs.
8 charges of 304 lbs. first coat	2432 lbs.
Total	7602 lbs. or 3.80 tons enamel mix

Fuel used: Franklin County R. O. M. at $2.75	$2.75
Freight	1.95
Unloading	.35
Wheeling coal to smelter, clinkering, handling ashes	.75
Total cost per ton to burn	$5.80
2.5 tons coal per 24 hours	2.5
Fuel cost per day	14.50
Cost per ton enamel mix smelted	3.81

One oil smelter will smelt 13 charges of 940 lbs. white or 12,220 lbs. per 24 hours. Fuel consumption 240 gallons.

Fuel 240 gallons oil at 5 cents	$12.00
45 kw. hr. for air, etc., at 2 cents	.90
Fuel cost per day for 6.1 tons enamel mix	$12.90
Cost per ton enamel mix smelted	$2.11

The above figures show the costs on the basis of the weights of enamel mix smelted. The figures given below are on a basis of 18% loss in batch weight or frit weight.

Comparative B.t.u. required and cost of frit.

Coal smelter (14,000 B.t.u. coal).	Cost	Oil smelter (142,000 B.t.u. oil)	Cost
1 Ton frit requires 1608 lbs. coal	$4.66	1 Ton frit requires 48 gal. oil	$2.58
1 Ton frit requires 22,512,000 B.t.u.		1 Ton frit requires 6,816,000 B.t.u.	
1 Lb. frit requires 0.8 lbs. coal		1 Lb. frit requires 0.024 gals. oil	
1 Lb. frit requires 11,200 B.t.u.		1 Lb. frit requires 3,408 B.t.u.	

These figures show a fuel saving of ($4.66 − $2.58) = $2.08 per ton of frit. In smelting 100 tons of frit per month, which is a fair average, an annual fuel saving of $2,500 would be realized. It is interesting to note that with coal at $5.80 per ton and oil at 5.373 cents per gallon, 100,000 B.t.u. costs 2.00 cents for coal, and 3.8 cents for oil. In other words oil costs 90% more on a strict heat unit basis. The fuel savings shown is possible due to increased furnace efficiency.

Labor Saving We have been able to save the labor of one man in the Smelting Department.

Saving Floor Space As the unit built has sufficient smelting capacity for some time to come the second unit of 2 smelters we proposed to build will not be built. The space used for coal storage is now used for productive purposes.

Conclusion

The oil smelters built are less complicated than the coal producer furnaces replaced, and consequently will cost less to maintain. These furnaces have a greater capacity than the coal furnaces replaced. We find it requires just one-half the time to reline these furnaces compared to our coal smelters. White frit containing 417 batches or 375,000 pounds was smelted with one lining.

An effective means of recuperation was devised which saves fuel and allows better furnace control. This was accomplished at a cost no greater than the cost of building an ordinary brick stack. Keeping the brick in the stack cool should prolong the life of the brickwork. We find flue temperatures running one smelter is 1310°F at the top of stack.

The uses of oil fuel for smelting has eliminated coal dust and dirt in the smelting department and adjacent factory space used for mixing, milling, etc.

Coonley Mfg. Co.
Cicero, Illinois

CORRECTION

Rebbeck, J. W., Mulligan, M. J., and Ferguson, J. B. "The Electrolysis of Soda-Lime Glass—Part II." *Jour. Amer. Ceram. Soc.*, **8** [6], 329 (1925). The ordinates of Fig. 3 should read 0.25 greater than they now do in all cases.

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ORIGINAL PAPERS

SOME OBSERVATIONS IN THE CASTING OF HEAVY ELECTRICAL PORCELAINS[1]

BY E. H. FRITZ AND A. L. DONNENWIRTH

ABSTRACT

A summary is given of experiences had in the manufacture of heavy and intricate electrical porcelains by the casting process. Some of the subjects discussed are selection and test of clays, mixing of casting slip and its control, and several details of the methods used in casting the ware. Special emphasis is placed on the limits established for viscosity and specific gravity of the casting slip and the general proposition that the slip must be within the limits set for viscosity regardless of specific gravity.

We have been casting heavy and intricate electrical porcelains for about two years. The process is undoubtedly more difficult to control and more sensitive to variations in clays than any other in the whiteware industry.

Variations in Casting Behavior of Clays

Successful casting depends primarily on the proper choice of clays. Most all clays will cast, but their manner of casting is radically different. We have fast casting clays and slow casting clays among both the china and ball clays. As a class the ball clays cast much slower than china clays.

Among the fast casting clays there are those which build up a firm solid wall from the mold to where the slip is casting and thus show a distinct change from slip to solid material. Others build up a firm cast adjacent to the mold but gradually the wall becomes flabby and soft as the slip is approached. The wall appears to be well cast but when the supporting molds are removed, it often is so weak due to its semi-solid condition that it collapses. The former type of fast casting clays are the most desirable but the latter can also be used just as successfully where the sections to be cast are not very heavy. We have had very little experience with slow casting clays for with them we have been unable to cast heavy sections. Possibly they could be used for lighter pieces.

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[1] Presented at the Annual Meeting of the AMERICAN CERAMIC SOCIETY, Columbus, Ohio, Feb., 1925. (White Wares Division.)

The classification of clays into these types can be easily made by the various methods which have been proposed, most of which employ a standard test piece to be cast and noting the casting behavior. To determine the cause of a clay's peculiar casting behavior is a more difficult matter. Grain size is a most important factor but it does not tell the whole story. We find that clays show considerable variation in casting behavior with no appreciable difference in grain size as indicated by settling. There are evidently other factors such as soluble salt content or a change in the nature of the colloidal material which affects this.

The Bingham Plastometer, like the settling test, will usually classify clays as to their casting value. We find that as a rule clays which show a low plasticity according to this test are the best casting clays. Plasticity tests do not, however, indicate the sometimes serious variations in a clay which alters its casting behavior.

We have read the suggestion of control of the hydrogen-ion concentration as a means of casting control. We have done some work on this test and are familiar with it. This test will undoubtedly give a measure of the amount of salts necessary for the slip, but we do not see how it can reveal a variation in the casting behavior of a clay which is not eliminated by a change in the amount of salts added. We will describe a variation of this kind in more detail, but it is well to emphasize at this time that this is the most difficult problem with which we have to contend in casting, and which so far has not been solved.

Relation of Design to Casting Rate

The designs which we are called upon to make limit us to clays which cast fast and solidly and which have low shrinkage in the mold. We have cast pieces where the wall varies from five inches to eight inches and in weight up to five hundred pounds, and we believe we can go further although it has not been necessary up to this time. For such work, the ball clay content must be kept as low as possible. We use no more than what is necessary to give the needed unfired strength so that the pieces can be handled without breaking. Eight to twelve per cent accomplishes this. As the ball clay is increased, the time of casting increases and the maximum thickness of section that can be cast is decreased. We have been able to finish the pouring of the largest pieces eight hours after it was started and the molds can be removed twenty-four hours after the pouring was begun. Such a schedule indicates the importance to us of low shrinkage of the body while it is in the mold, and this is another factor which is considered in our choice of clays.

Preparation of Slip

In preparing the clay slip for casting, all the ball clay, china clay and scrap is placed in the mill, with sufficient water and sodium silicate for the entire charge, and ground for forty-five minutes. The amount of water and silicate is determined by the amount used in the previous charge, the water being measured by means of a meter and the silicate accurately weighed. To this is added the feldspar and flint and the entire charge is ground for thirty minutes more.

A check is made at this time, before the mill is emptied, on the viscosity and specific gravity and corrections are made, if necessary, to make the slip suitable for casting.

Testing of Slip

The viscosity is measured by the flow type viscosimeter and is expressed in the number of seconds required for 100 cc. to flow through an orifice $^7/_{32}''$ in diameter. We do not use a lid on this viscosimeter, which enables the test to be made more rapidly; but on the other hand a slight error is caused due to the difference in pressure, as the height of the slip decreases. By always filling the viscosimeter to the same point, however, the results are correct for comparative purposes.

For specific gravity determinations, we use a small necked bottle which is calibrated so as to express the weight in ounces per quart. This we find, to be much more accurate than a pint or quart measure.

The viscosity of the slip, before it is emptied into the cistern must be between 40 and 65 and the specific gravity must be 60.2 ounces per quart. These limits were established after some experimenting and also upon observations made in the casting shop, which will be described later.

The slip in the mill, after being checked, is passed through a thirty-mesh lawn into a storage cistern, where it is kept in motion continuously by an agitator.

Limits of Viscosity and Specific Gravity

Every morning the slip in the cistern is again checked before using. The viscosity must lie within the limits of thirty-five to fifty-five. It will be noticed that these limits are ten points lower than the limits set for the slip as it is checked in the mill, but we find that by agitating the slip over-night, the viscosity is lowered to this extent. This is due, probably to the fact that the grinding time being so short, the point of maximum deflocculation is not reached until the slip is further agitated. As an illustration of this, some time ago we made up a slip having a weight of fifty-nine ounces per quart and a viscosity of forty. Blunging for eight hours additional reduced the viscosity to thirty-three, all other factors remaining the same. Continued blunging for sixteen hours reduced the viscosity to twenty-seven, but blunging for a longer time had no effect.

When we first started casting, a slip weight of 60.5 ounces per quart was maintained, and we were of the opinion that we could not change this weight, especially decrease it without encountering trouble such as excessive shrinkage. Everything went along fine for a time, until a change was noticed in that we could not maintain the proper viscosity, regardless of the amount of silicate used. The slip acquired a very sluggish appearance, the length of time required for casting increased and the slip would hang up in the mold, which prevented solid casting, causing what is termed "balling." In casting very thick and heavy pieces, we found on removing the side walls and core that the piece of ware would be so weak that it would sink down under its own weight indicating a soft flabby cast which, however, appeared solid.

We decided it was necessary to use a lower viscosity and there was only one way to accomplish this, and that was to lower the specific gravity. By reducing it to 60.2 ounces per quart, the viscosity dropped to within the limits and the trouble just described disappeared. The reduction in specific gravity was not sufficient to give any shrinkage trouble, and we have therefore used this weight since that time. This experience led us to believe that the viscosity is more important than the specific gravity and that the specific gravity should be reduced, if a satisfactory viscosity cannot otherwise be obtained. We are using this theory as a basis of our slip control and so far have had very satisfactory results. We believe that it is desirable to have a viscosity as low as possible at all times at a given specific gravity, but it is necessary that we set a lower limit because of settling. A viscosity below thirty-five will cause the heavier particles to settle more or less. In other words, we seem to encounter this before maximum deflocculation is reached.

It is, of course, understood that the specific gravity value should be set as high as possible, without exceeding the viscosity limits, on account of lower shrinkage and faster casting time. The important point, however, is that we reduce the specific gravity, if necessary to bring the viscosity to the proper value. When this is necessary a decrease of from .1 to .2 ounce per quart is usually sufficient to lower the viscosity from ten to twenty points.

Amount of Electrolyte Required

The amount of electrolyte required, often varies from day to day and over a period of six months fluctuated between 800 grams and 2200 grams. This is to be expected, however, and is probably due to a variation in the soluble salt content of the clays used.

Recently we received a car load of china clay which appeared to be no different from any previous shipment, but on using it we encountered quite a bit of trouble. It was possible to bring the slip within the limits for viscosity and specific gravity, but the casting behavior was changed decidedly. It had a sluggish appearance, cast slower and hung up in the mold somewhat, making it difficult to obtain a solid cast in the heavier designs. It resembled the slip we were using when we were trying to maintain too high a specific gravity. This condition was improved slightly by maintaining a viscosity very close to the lower limits, but could not be entirely eliminated. Upon the arrival of another shipment of clay, the trouble disappeared.

There was evidently some difference between these two lots of clay, but up to the present time we have been unable to find a test which indicates it. A plastometer test or a settling test, as mentioned previously, showed a slight difference but not sufficient to segregate the clay which gave trouble from that which we know was satisfactory. It is a serious condition and we hope that a solution or helpful suggestions are offered by those who have had similar experiences.

Method of Casting Open top molds are used entirely. They are so superior to the funnel type that no other choice is possible. The slip is supplied by the continuous pump circulation method. This has been very satisfactory and seems to have no effect on viscosity. A ten-foot length of eight-inch pipe or a tank of some kind must be inserted in the line between pump and outlets to eliminate pulsation. The pipe lines are cleaned every evening with compressed air, to eliminate any chance of clogging.

Both core and drain casting are done, although the bulk of the work is by the former method. To facilitate release of the cores, an application of talc or compressed air is used. The former is more simple but not quite as effective and cannot be used when the cores are large and the taper not great.

For designs of variable thicknesses where wide sections occur in the lower part of the mold, it is necessary in pouring to fill the mold only in part, at first, thereby casting the wide section before any casting is done on the narrower sections above. Additional pours, must of course be made, before the top of the preceding pour has become too hard to unite.

We have tried to give a general idea of our casting methods, bringing out difficulties we have had and are still having, as well as those things we believe we have fairly well in hand. We have incorporated this information in a process specification which has been issued to the shop for their guidance and which cannot be changed without the ceramic engineer's approval, insuring definite control. We expect that it will have to be revised, perhaps frequently in the future, for casting is still new with us and we hope that as we progress, further improvements will be obtained.

THE WESTINGHOUSE HIGH VOLTAGE INSULATOR CO.,
LATROBE., PA.

Discussion

E. H. FRITZ: We have been unable to find any test that will indicate the variation which we sometimes (not very often) encounter in clays that we use.

W. L. SAMPLE: Do you take into account the difference in temperature of slip from time to time? That would give a different viscosity reading. In our plant we have quite a difference in temperature of the slip. On a cold day the slip will be quite cold and vice versa.

A. L. DONNENWIRTH: We do have variation in temperature. It varies from about 65° to probably 85°. This has a slight effect on the viscosity, but we take that into consideration.

W. L. SAMPLE: Do you have a graduated chart that shows that?

A. L. DONNENWIRTH: Yes.

CHAIRMAN MCAFEE: Speaking of differentiation in clays, do you make a viscosity test on clays or do you make viscosity tests on your slips? There might be some advantage to you in differentiating that.

E. H. FRITZ: The plastometer test referred to in the paper is something similar to that.

R. A. HORNING: That does not indicate this variation that you have. I thought a viscosity test was made on the clays before sodium carbonate was added.

R. W. HEMPHILL: We tried out the clays separately by casting them instead of this other test where they are put in a tub and are shaken up. Does that make any difference: to test out the china clay and see how long it takes, how much water, and if that varies any?

E. H. FRITZ: That might indicate the difference but what we are also after is why we have that difference. What is in the clay that causes that difference? If we know that we can test for it quantitatively and possibly be able to make adjustments for it.

C. W. PARMELEE: Perhaps Mr. Fritz has not taken into account the organic content of the product.

E. H. FRITZ: Probably not, but we have not had any trouble which we could trace to the ball clay. The china clay we use is English china clay and contains practically no organic material.

C. W. PARMELEE: What is the effect of time on that slip, a slip which is made today and not used for twenty-four hours or more? Have you noticed any material changes in the viscosity conditions or other conditions?

E. H. FRITZ: A minimum viscosity was reached after sixteen hours. But that would not necessarily be the same. You would reach maximum deflocculation sooner at one time than another.

A. S. WATTS: Were these results obtained from china clay which came uniformly from the same mine?

E. H. FRITZ: Yes.

A. S. WATTS: A short time ago the statement was made to me that some English clay miners at the present time are bleaching their china clay with a dilute solution of blue vitriol. I am wondering whether it could be possible that the presence of some bleaching agent would account for such a thing as this in regard to the behavior of the clay.

When I was in England I saw a lot of extremely blue water in the bottom of the clay mine, but I assumed that it was just the normal color of clear spring water intensified by a certain amount of clay in suspension, and I rather question whether there is anything of that sort used in the bleaching of English clay.

I do not pretend to know anything about the bleaching that is done in English china clays, but I raise the question in order to elicit information if there is anyone here who can tell us anything about it.

R. REIF: We had a carload of English china clay shipped to the plant. It was chalky and had a great tendency to crumble in my hand. We received another car some time later, same clay, same concern, but this clay was fatty and greasy. The chalky stuff would not work but the fatty stuff would. They had practically the same fineness. Can you explain it?

E. SCHRAMM: Did the clay have the same moisture content?

R. REIF: There was a difference of moisture content of one per cent.

E. SCHRAMM: Was there any chance of the one lot having been frozen?

R. REIF: Both came in about June or July.

H. GOODWIN: Do you use the china clay in the raw state or do they put it through a filter press?

A. L. DONNENWIRTH: We use the china clay in the raw state.

E. H. FRITZ: Would it be possible that contamination of the clay by ocean water on the way over might have something to do with that variation?

A. S. WATTS: There would not be very much opportunity for contamination unless the compartments become damp with sea-water.

E. H. FRITZ: We know of cases where there has been leakage in the boat.

A. S. WATTS: That may be possible. The sodium chloride would act very definitely, but I had never taken that into consideration because such an impurity would be abnormal.

A few years ago a large shipment of clay was put into the hold of a steel compartment vessel. The compartment had not been properly cleaned and a certain amount of iron rust was there which caused much argument.

CHAIRMAN MCAFEE: The point was brought out in the discussion on the English versus the American clays that at one time Mr. Brian found them slushing the ball clay down chutes into the boat, but he did not mention whether they used sea-water to slush it down or fresh water. However, I do not believe that is a common practice. It might possibly explain some variation in ball clay in case they use brackish water for that purpose.

E. H. FRITZ: For the casting process we have not been able to get an American china clay that will cast the very thick sections that we have to cast. It is possible to cast thinner sections with the American china clay but not sections over four inches. We have had no difficulty whatever with American ball clays. We use no English ball clay in our cast body.

A. S. WATTS: Some of the English china clay plants are filter pressing their clay and some of them are still putting it on top of the driers, a tile floor where the water is dried out. There would be a certain appreciable difference. If you were buying from a concern that was drying part of the clay by one process and part by another, that would undoubtedly introduce an error

H. GOODWIN: On the whole the English china clays are fairly moist when they leave the mines. Some of them are kiln dried and they are apt to get a little drier than those otherwise dried. However, I do not think that any absorption would take place which would affect the body.

There is no possibility, except in rare cases, of any salt water getting into the clay, because if there was leak in the boat of any amount the clay would be "soupy" when it was delivered and you would know there was something the matter. The boat people on the whole take very good care to keep the clay dry. They even go so far as to discontinue discharging when there is the slightest amount of rain at the docks.

SLIP MAKING AND CONTROL[1]

By Paul H. Sanborn

ABSTRACT

The properties of slip for casting solid pieces are discussed. Difficult control of slip and blistering are eliminated by use of an organic electrolyte. The effects of variations in specific gravity, viscosity and temperature are considered.

Introduction

The following discussion is based on observations made on slip for casting solid pieces used in the manufacture of electrical porcelain.

In a great many instances various troubles such as blistering of fired ware, difficult drying, and slow casting can be traced directly to the treatment of the slip. A few of the variables encountered in the preparation of slip and the effect of each will be discussed.

The Effect of Viscosity

It has been observed in practice that slips of high viscosity cast very rapidly, and that the time of casting increases as the viscosity decreases. When solid pieces are cast with slip of very high viscosity the portion of the slip in contact with the mold will cast very fast. This part will shrink away from the mold leaving an excess of water in the center. This results in a piece of varying density which will often crack in the drier due to the increased amount of water which must be removed.

The time of casting is considerably increased when slips of low viscosity are used. However, more uniform and dense ware is obtained. When the viscosity is very low the casting is much slower. There is also a tendency for the non-plastic materials to settle when large pieces are cast. Drying is more difficult when slip of this kind is used.

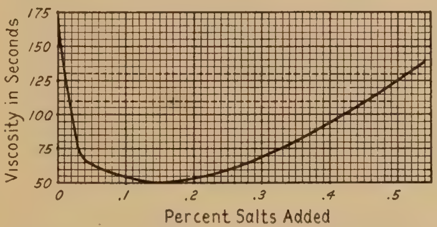

Fig. 1.—Viscosity curve 1:1 sodium silicate and sodium carbonate. J. D. I. Co. Sp. gr. 1.80.

The Use of Electrolytes

The addition of electrolytes is one of the most important steps in the preparation of slip. (Fig. 1.) This curve shows the effect of an electrolyte which consists of a 1:1 mixture of sodium carbonate and sodium silicate. The first additions cause a very rapid drop in viscosity after which the effect becomes less. Further additions cause a more gradual rise.

The parallel lines represent the limits of viscosity which give the most satisfactory results. It is possible to obtain the same viscosity at two points on the curve. However, the properties are quite different. The portion of the curve at the left is the one used in general practice.

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[1] Presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, Feb., 1925. (White Wares Division.)

Slow casting and drying are encountered when slip corresponding to the portion of the curve at the right is used. In drying, the water containing the salts in solution, moves to the outside of the ware, and is evaporated, thus leaving the salts concentrated at the surface. This is one of the most common causes of blisters. The quantity of salts is sufficient to cause a decided fluxing action on the body. The life of the molds is shortened by the action of the salts.

The desirable working part of the curve is very steep, consequently small change in concentration of the electrolyte will bring about a relatively large change in viscosity. Obviously it would be a difficult matter in practice to adjust the concentration of the electrolyte to bring about the desired condition. This is accomplished by the use of a Missouri clay of unusual characteristics. This clay contains a natural electrolyte of an organic nature, the effect of which is extended over a period of time. In the particular process used, the slip when made has a viscosity of about 180. It is then aged for a period of four days. During this time the viscosity will drop to about 125, at which point it is ready for use. This change is brought about without the addition of any deflocculating agents. If the viscosity drops below the lower limit, it is only necessary to add a very small amount of a flocculating agent.

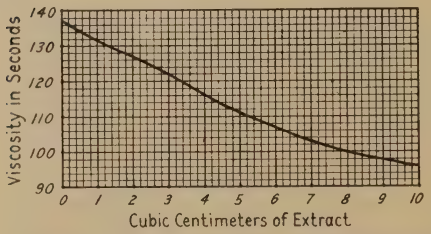

FIG. 2.—Viscosity curve. Missouri ball clay extract slip—600 cc. 1.80 sp. gr. Extract—5 grams lignite boiled 5 minutes in 200 cc. distilled water.

The Missouri clay contains a large amount of lignite. This lignite seems to contain most of the electrolyte in the adsorbed state. When five grams of the lignite was boiled in 200 cc. of water for five minutes, the extract was found to have a pH value of 8.0 (Fig. 2). This curve represents the change in viscosity with the addition of the extract, showing the deflocculating properties which the clay has. The effect of this electrolyte can be adjusted to meet different conditions by varying the amount of the clay. This clay can be substituted for china clay. An electrolyte of this type is very desirable. It is readily oxidized in firing and leaves nothing to exert a fluxing action or to cause blisters. The effect on the molds is very slight.

The Effect of Weight

If the specific gravity of a slip is high an excessive amount of electrolyte is required to bring it to the proper working condition. The action toward electrolytes is often very erratic. Slip which is too light will delay the time of casting and will be difficult to keep in suspension. The proper weight of slip can only be determined by experiment.

The Effect of Temperature

Viscosity is greatly affected by temperature changes (Fig. 3). The speed of flow of the water through the body is a function of the temperature. The proper temperature of slip for casting can be determined by experiment.

In attempting to control slip it is necessary to take into consideration all the factors which enter into the preparation. A variation in one will cause variations in the others. The best method seems to be that of holding as many as possible at a constant value. If the weight and temperature can be held constant the viscosity can be adjusted with some degree of certainty by means of electrolytes.

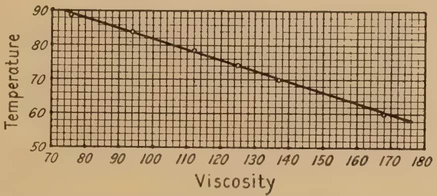

FIG. 3.—Viscosity *vs.* temperature. Sp. gr. 1.80.

The weight of the slip is taken by means of a 500-cc. volumetric flask, which has the neck removed at the graduation line. The flask and the slip are weighed in grams and a table consulted, giving the weight in ounces per pint. The specific gravity is easily obtained from the same figure. This method gives good results in the hands of the workmen as the chance for error is small. The viscosity is taken by means of a viscosimeter which has an arbitrary scale. A viscosity of 100 seconds represents the danger line and requires immediate correction. By having this standard to work from, the men are able to appreciate the effect which the viscosity has.

THE JEFFERY-DEWITT INSULATOR CO.,
KENOVA, W. VA.

Discussion

C. C. TREISCHEL: The question of control of the casting slip is no doubt one of the most important questions in the proposition of casting.

K. M. SMITH: What is the meaning of the term that pH is equal to 8?

P. H. SANBORN: The pH value represents the concentration of the hydrogen ion, or in this case, the hydroxyl ion. It is obtained by two methods. One requires quite an elaborate array of apparatus, the electrometric process; and another is by means of the colorimetric process, which has the disadvantage of requiring a very clear solution in order to observe the colors.

The electrometric process or method is very much more accurate because turbid solutions can be used. However, the apparatus is very expensive, and you want to be sure that you have a need for it before you get it. That measurement was made in order to determine the character of the extract of this ball clay. The other ball clays which we use show a slight acid reaction. Hydrogen-ion concentration of seven is the neutral point. A concentration of pH value of 8 represents slight alkalinity. It is a very accurate means of determining the slight alkalinity or acidity of any solution.

E. H. FRITZ: Would the hydrogen-ion concentration determination indicate the variation in the clay which we spoke of in our paper? We stated that we did not seem to be able to take care of it by trying different amounts of electrolyte. That was a "cut and dried" method, however We tried various amounts of electrolyte. We were able to lower viscosity with increased electrolyte, but this did not eliminate the trouble. Higher viscosity did not correct the condition either.

L. NAVIAS: $H_2O = H^+ + OH^-$. The water dissociates into hydrogen and hydroxyl ions. In other words, water contains these two ions and the Law of Mass Action states that the hydrogen ion and the hydroxyl ion are contained in equivalent amounts at equilibrium. It is a fact that at room temperature of roughly 22°C the concentration of the hydrogen ion and the hydroxyl ion in the water has the value of 10^{-14}, and therefore each of the concentrations, that is, of the hydrogen ion and of the hydroxyl ion, will be 10^{-7}, as the water breaks up into hydrogen and hydroxyl ions of equivalent amounts, and this (10^{-14}) expresses the total value of the dissociated water present. So that the neutral point in this equilibrium really means that there are as many hydrogen ions as there are hydroxyl ions and under those conditions the neutral point will have the value of 10^{-7}.

If we add an acid to the water solution, as HCl which dissociates into hydrogen ion and chlorine ion we will be increasing the concentration of the hydrogen ion and decreasing the concentration of the hydroxyl ion, but the equilibrium constant will always remain the same. In this manner we can increase or decrease the hydrogen ion to any value at will. 10^{-7} is the hydrogen-ion concentration. The pH value is merely another way of expressing it, namely, as the logarithm of the reciprocal of the hydrogen-ion concentration, $\log \frac{1}{157}\cdot$ The pH value in this case would be 7, and the increase in this value, say, to 8 would actually mean a decrease in the hydrogen-ion concentration.

P. H. SANBORN: Mr. Fritz asked a question about our application of this method of measurement. I will have to say that it does not tell the whole story. There are a number of other factors that must be taken into consideration. However, if used in connection with viscosity you can pretty well tell what to expect the viscosity to be by the treatment with certain electrolytes.

H. GOODWIN: What percentage of this was ball clay?

P. H. SANBORN: We use a mixture of two ball clays. We vary it according to temperature conditions. In the summer time we cut down on it a little bit and in the winter time we can increase the amount. We can get where we want to on the viscosity by the proper judgment of this clay since it carries its electrolyte with it.

C. C. TREISCHEL: Would a body of the particular type which Fig. 1 represents, if deflocculated with an inorganic deflocculating material cast better in this range here between the parallel lines?

P. H. SANBORN: Yes, regardless of whether it is organic or inorganic. That seemed to be the best range, the one within the parallel lines.

C. C. TREISCHEL: As a slip is deflocculated within this range (25 or 30) ages, will it tend to get thicker?

P. H. SANBORN: No, the slip will get thinner, the viscosity will become lower as it ages.

C. C. TREISCHEL: If deflocculated with inorganic material?

P. H. SANBORN: If inorganic material is used it will drop in viscosity for a certain period of time, after which it becomes set or begins to thicken. The viscosity becomes higher.

C. C. TREISCHEL: Is the reason for the dropping a matter of not mixing it long enough in the blunger before it goes into the agitators?

P. H. SANBORN: Yes, that is probably the reason.

C. C. TREISCHEL: Then am I right in assuming that with your method of deflocculating with the organic material, you deflocculate over on this side of the curve? (Right side.)

P. H. SANBORN: We try to keep away from that part of the curve. If during our process of aging the viscosity drops below the lower limit there, or the lower parallel line, we will add acetic acid or some similar flocculating agent to bring it within the bounds.

C. C. TREISCHEL: If you get down below this point and add acetic acid, then am I not right in assuming that you thoroughly deflocculate your clay in the preliminary mixing.

P. H. SANBORN: We add no sodium carbonate or silicate or any other deflocculating agent to the slip at any stage, so at the time it is made it will have a viscosity of about 180, and during the period of the four days aging the viscosity will drop close to the range between parallel lines.

C. C. TREISCHEL: I cannot get your point of view. It may be because it seems to me that with what you do and with the answers which you have given to my questions you must be over in this range in deflocculation rather than in here with your organic materials. And as it ages it gets thinner by coming down this curve here, so that if you come below this point and a flocculating material is added, such as acetic acid, you would throw yourself over on this side of the curve.

P. H. Sanborn: If you had the slip at the end of the four-day period and the viscosity went down, you could be pretty sure you were on the left hand side of the curve, could you not?

C. C. Treischel: Yes.

P. H. Sanborn: Well, that is what happens.

C. C. Treischel: You are here (left side) then. I was wondering whether you were over here on the right side, and if you were, whether there was any difference between the casting action on the left side and the right side.

P. H. Sanborn: We have used slip on both sides. In order to tell which side of the curve we are on we take the slip and add sodium carbonate, and if the viscosity goes down, we know we are on the left hand side, and if it goes up we know we are on the right hand side.

C. C. Treischel: Are the results the same?

P. H. Sanborn: No, the results are quite different.

A Member: May we ask what sort of ware you cast, please?

P. H. Sanborn: We are casting high tension insulators in open top molds. They weigh about 33 pounds apiece. We make three pourings per insulator. It is very necessary that we get the proper bond between different pourings. While we were operating on the right side of the curve we found that a decided scum showed up which interfered with the bond. That was due to the increased amount of salts which were concentrated there on the top due to the evaporation of the water which prevented the best bond between the different pourings. However, on the left side of the curve, we are entirely free from that scum and the different pourings are bonded properly.

C. C. Treischel: It is quite evident then that the deflocculating action of the organic material is much slower than that of an inorganic material.

P. H. Sanborn: Yes, it is not very rapid. It stands over a period of over four days. It takes a four-day period to get the viscosity which we desire.

E. H. Fritz: Why is the lower limit set so far above the point of maximum flocculation? Would it be desirable to go down as far as 75? You would still be on the left hand side of the curve. What trouble is encountered in doing that?

P. H. Sanborn: We allow ourselves a good margin above the settling point. The slip will settle in the neighborhood of 80 viscosity.

E. H. Fritz: Do you encounter settling before maximum flocculation is reached?

P. H. Sanborn: Yes.

F. S. Hunt: Casting is not one of our problems, but in working with sodium carbonate and silicate in factory conditions it is almost next to impossible to work with a slip that high up on that curve. Most people are working, I believe, down at that 75 point and have a chance to keep it somewhere uniform. A slip up on that part of the curve is very much more subject to variation than one down further on the curve, unless this ball clay acts differently than sodium carbonate and sodium silicate.

C. C. TREISCHEL: I think there is one thing Mr. Sanborn has brought out with respect to that, and that is that it is much less active. The action is much slower and extends over a period of days while the inorganic deflocculating material takes effect in a matter of a few hours. There is a difference there.

E. H. FRITZ: That is an individual condition depending on what is being cast and how the viscosity is determined. Our viscosity limits are very low numerically. Very likely our viscosity is not any different from Mr. Sanborn's; it depends upon what kind of ware is being cast.

F. S. HUNT: I was bringing out the point that you are trying to work that on that curve of viscosities.

E. H. FRITZ: I meant that, too.

W. K. MCAFEE: I would like to hear this discussed from another view than that of electrical porcelain. Our own experience in casting control is that the viscosity readings are not reliable so far as we are concerned. We work specific gravity the same and test the action of the slip in actual test cast. Our viscosity varies greatly, and does not seem to prove anything so far as our own particular process in casting sanitary ware is concerned. We do not pay any attention to viscosity.

P. H. SANBORN: With this particular body used here, which has a ball clay content of 6%, and since the settling point occurs as a viscosity much above the point of maximum deflocculation, it is necessary to pay very close attention to the viscosity.

C. C. TREISCHEL: With a low ball clay content it is much more likely to settle than one having 15% or 20% ball clay.

W. K. MCAFEE: I would like to have that side of the argument brought out by some discussion.

C. B. YOUMANS: We are casting sanitary ware and about three or four months ago we tested for specific gravity and held to that, but then we thought we would try something else along with specific gravity and we tried this viscosity, and we found that had a great deal more to do with the casting than specific gravity. We can vary specific gravity possibly one or two grams but if we vary in viscosity as much as two or three minutes it will throw us way out. Since then we have been trying to hold to a viscosity instead of a specific gravity.

W. K. MCAFEE: I did not mean to convey the impression that our viscosity varied quite that much.

C. B. Youmans: We have ours vary as much as two or three minutes and when we do we are in a lot of trouble, but we can cast within a minute's variation and have no trouble at all.

W. K. McAfee: That is the same point I wanted to bring out, that it could vary over a considerable range. We have found that specific gravity needs to be kept fairly uniform for our particular method.

E. Schramm: What is the percentage of change represented by two or three minutes?

C. B. Youmans: If we come down to two minutes for 200 cc. we can still cast with three minutes for 200 cc.

K. M. Smith: Do you find that the man making the slip can determine the viscosity a great deal by pouring the slip, or by feeling of it with his fingers?

C. B. Youmans: We are working on such a heavy schedule, we do not have time to try all of these little individual tests. We are making about 40 to 50 tons of slip a day, and we are working on such a fast schedule that we do not test every batch. We only test in the agitator once a day, usually in the morning before we start.

K. M. Smith: We have an Italian making the slip up at the other plant and he can judge the viscosity very nicely by blowing on the slip. He makes very good slip.

E. Schramm: In a great many potteries that manufacture whiteware it is left to the workmen to a certain extent because the slip is not delivered and controlled. It is delivered in tubs, some is used and then it stands around until more is put in it. No one has ever devised a way of avoiding that situation. We control our casting slip as we make it, but beyond that it is out of our hands. We have never felt at liberty to forbid the men making adjustments, especially on the specific gravity of the slip. We feel that we have to rely on their personal skill in the last analysis.

E. H. Fritz: Was any difference ever noticed in casting the slip which had a viscosity which was high where the specific gravity was all right?

W. K. McAfee: If the viscosity gets too high, that is, beyond the limits suggested by Mr. Youmans, of course, it does not drain right in hollow casting or over-casting, but up to that point where it does not actually drain right in the mold, it does not make a great deal of difference. It will have some effect on drying and setting up, but the temperature and mold variations seem to make more difference than that. As compared with the other variations that enter into casting, viscosity does not seem to be so important.

E. H. Fritz: What would you do if the specific gravity was satisfactory but the viscosity was not?

W. K. McAfee: We would probably add more salts to bring it down because we seem to be high enough up the left hand side of the curve to make that correction. We are frank to say we do not know very much about making slips so far as technical control is concerned.

E. T. MONTGOMERY: I would like to ask Mr. Fritz if he uses gravity or forces the slip out by air pressure.

E. H. FRITZ: By gravity.

E. T. MONTGOMERY: Do you empty through a pipe line or valve?

A. L. DONNENWIRTH: We empty the mill through a valve by gravity. Air pressure is used in addition to merely speed up the operation.

E. T. MONTGOMERY: If air is used it brings in another factor which would affect the use of the ball mill as a viscosimeter. That is the reason I asked the question. When emptied by gravity and through a valve I was wondering if you found the ball mill to be rather an accurate viscosimeter itself. If your mill will empty properly have you still the possibility of too great a variation in the viscosity?

A. L. DONNENWIRTH: You can notice a difference in the viscosity. If it is too high it takes a much longer time to empty the mill.

E. T. MONTGOMERY: Is the ball mill a sufficient guide, or must you make a test with a viscosimeter?

A. L. DONNENWIRTH: We have never used it as a guide. We always make a test with a viscosimeter.

E. T. MONTGOMERY: I have found in my practice in making very small quantities of slip that the rate of flow from my ball mill is a sufficient test for me.

A. L. DONNENWIRTH: When the mill is finished we take a small sample. It only requires about two minutes at the most to make that test, so you see we do not waste much time and it is much more accurate.

E. T. MONTGOMERY: Except that you are dealing with a small quantity and perhaps the test on the larger quantity might be even more practical than that and of equal value. That is the point I had in mind.

E. H. FRITZ: I do not believe it would be close enough.

K. M. SMITH: I would like to ask Dr. Navias if it would be possible to dilute a slip down with distilled water and then add a color such as methyl orange and titrate with a known solution. What kind of a factor would you use to convert it over into a hydrogen-ion concentration?

L. NAVIAS: The soil chemists have done a great deal of work along these lines using the colorimetric method for their pH concentrations.

K. M. SMITH: What color do they use?

L. NAVIAS: They have a series of indicators. There are quite a number of organic acids or bases which exist in tautomeric forms in equilibrium with each other in solution. They also have the property of changing their color at the transformation corresponding to a definite hydrogen-ion concentration. That is what is used in the colorimetric method.

For instance, phenolphthalein is a good example. At a definite pH value, that is, at a definite hydrogen-ion concentration it changes from colorless to red. This is purely a comparison method standardized by the electrometric method. The pH value for the change in color is determined once for all, and so it is just a matter of finding a number of organic compounds of this type with values which are spread over the field.

Washburn has taken a number of salts of organic compounds and plotted them in a curve of this type in which he gives the name of the salt, and also the pH value at which it will change from one color to another, and you can find that published in quite a number of hand books.

The soil chemists, of course, have made a big study of the indicators. Dr. Clark of Washington has done a great deal of work along these lines. It is just a matter of getting together a number of suitable organic compounds that will be converted, one at a pH value of 7, another at 8 and another at 9, or intermediate values, and using the series for the determination. In the actual determination it is just a matter of taking the water solution of whatever material you are dealing with and adding known concentrations of your indicators to it under control conditions and noting where the change takes place.

There is a very fine method discussed in the literature[1] whereby one can determine the intermediate values between the color changes by a comparison method. One set of test tubes containing different quantities of indicator is made alkaline, while another set is made acid. The color of the indicator in the unknown solution is then compared with the intermediate colors obtained by coupling the "acid" and "alkaline" standard indicator solutions.

K. M. Smith: May I ask where and to whom to write to get this information and if this series is set up in shapes so that a person can buy standard solutions?

L. Navias: Yes, you can. I am not advertizing anything but I might mention off hand a company, I think it is the La Motte Company, which produces a series of indicators ready for use.

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[1] "Colorimetric Determination of H-Ion Concentration without Buffer Mixtures, with Especial Reference to Soils," Louis J. Gillespie, *Soil Science*, **9**, 115–36 (1920).

SYMPOSIUM ON CASTING PROBLEMS[1]

Question 1 Is a higher firing temperature or a longer soaking period required to accomplish complete vitrification of a cast body, compared with the same body used in plastic form? (By G. W. Lapp.)

C. C. TREISCHEL: I know of some who have used the same body exactly for casting that they do for wet process.

C. S. MADDOCK, JR.: We use the same body for casting that we do for pressing. We have made no change in our firing conditions because we see no difference in the firing of the cast or the pressed ware.

F. H. RHEAD: The type of ware and clays used should be considered in answering this question. Why not cast and press a similar shape with the same body, firing these in the same sagger at a temperature approximating vitrefaction?

Absorption tests could be made, and if the cast piece proved to have higher absorption than the pressed piece, it is reasonable to assume that a slightly higher firing temperature or longer soaking period might be necessary to accomplish the complete vitrification of a cast body compared with the same body in plastic form. It should be obvious that different mechanical treatments in connection with clayworking processes would more or less result in physical differences in the bodies when subjected to the same firing conditions.

Assume that a typical earthenware or sanitary ware body was used in making a round disk exactly eight inches in diameter and $^1/_4$-inch thick (mold size) by the following processes:

A. Dust pressed. Moisture content 10%. Pressure 500 lbs.
B. Dust pressed. Moisture content 15%. Pressure 3000 lbs.
C. Cast, without salts, 24 ozs. to the pint.
D. Cast, deflocculated slip, 32 ozs. to the pint.
E. Pressed, moisture content, about 25%.
F. Jiggered, moisture content, about 30%. Ordinary knife edge jigger tool.
G. Jiggered, moisture content, about 30%. Flat heel wooden jigger tool.

and that these slabs were all fired in the same sagger until the average absorption would be about 3%. When the slabs came from the kiln and were measured it would be found that there would be a variation of from $^1/_{16}$ inch to at least $^3/_{16}$ inch in diameter, and that the absorption would vary at least 1%.

In casting heavy clay products there is sometimes enough weight and pressure combined to offset any marked physical differences between cast and plastic processes as far as contraction and absorption are concerned. But this again depends on the particular treatment and composition of body.

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[1] Presented at the Annual Meeting, AMERICAN CERAMIC SOCIETY, Columbus, Ohio, Feb., 1925.

H. Goodwin: Due to our disastrous fire and complete destruction of scales, I cannot arrive at any definite conclusion. However, you can assist to some extent, so I am sending you by Parcel Post two pieces marked "C" and two marked "P" at the time they were made and dried. The pressed pieces were as I recall somewhere about one ounce heavier (avoirdupois).

I would suggest that you weigh these four pieces, then determine the absorption. This will show the relative density difference between a cast or a pressed piece. Orton cones 6, 7 or 8 were fired with these pieces, and Veritas disks, and although one piece marked "C" and one "P" were fired in the same sagger there is no difference in points registered by the disks. Sometime later it may be possible to pursue this study further.

Report by A. E. MacGee:[1] The dry weight of the two cast bowls is 504.3 and 489.5 grams respectively. The dry weight of the two jiggered bowls is 515.0 and 547.5 grams respectively.

The porosity of the two cast bowls is 22.67% and 20.86% respectively. The porosity of the two jiggered bowls is 20.08% and 19.75% respectively. The porosities were determined after soaking in distilled water for 1$^1/_2$ hours, boiling 1 hour and standing 17 hours. The dry weight, saturated weight and suspended weight were taken.

C. C. Treischel: It would seem then that the amount of alkali that is used for deflocculation has no effect whatever upon the maturing temperature of a body.

R. W. Hemphill: We make cast ware out of the same body as is used in pressed ware, firing the cast in the bottom part of the kiln. The dry press has to be placed higher. The cast ware will vitrify in the bottom of the kiln. The same body by wet process has to be fired harder.

C. C. Treischel: Have you any idea in percentage how much alkali the body uses?

R. W. Hemphill: No.

C. C. Treischel: Ordinarily on the basis of half soda ash and half water glass about 0.4% is what is used. If you are going higher than that the concentration of alkali might play some part.

R. W. Hemphill: About 100 ounces of alkali to 1600 pounds of clay, I believe.

C. C. Treischel: The alkali percentage then is about 0.4%.

W. K. McAfee: I have had no personal experience, but a plant that we took over was formerly using the same body for casting and pressing sanitary ware. They reported that the cast ware was fired harder through the same firing conditions in a tunnel kiln than the pressed ware. It was apparently vitrified a little bit more. You could tell the difference in the color and in the ring of it.

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[1] July 14, 1925.

T. W. BLACK: I have found where I have used colored slips on cast ware that the colored slips vitrified quicker than they did on pressed or other ware. I do not know whether the electrolytes in the cast ware have any effect or not, but it appears that they have.

Question 2 To what extent do electrolytes used in preparing casting slips replace feldspar and other fluxes in completely vitrified bodies?

C. C. TREISCHEL: This was discussed in the first question.

Question 3 How do the drying shrinkage, firing shrinkage and maximum density of a cast body compare with these properties in a similar body made up in plastic form?

C. S. MADDOCK, JR.: We do not notice anything in the body. We use a slip of 32 ounces to the pint and can find no appreciable difference between the cast and the pressed ware. The cast body will be a little bigger.

M. R. HORNUNG: We do not differentiate between the drying and firing shrinkage, but their total will be smaller with the cast piece than with the pressed piece.

C. C. TREISCHEL: That is with a slip of what weight?

M. R. HORNUNG: The slip is about 30 ounces or perhaps 29. That is for china.

Question 4 What measures should be taken for correcting a slip that requires excessive electrolyte?

C. C. TREISCHEL: If we should consider that a slip for casting would normally contain about 0.4% alkali, based on materials used, how could we correct a body which requires 0.6% for deflocculation; what changes could we make in that body to get it down to 4%?

A. FOLTZ: Some of us have never had any experience with a body that required that.

C. C. TREISCHEL: Suppose you are using 0.35% of alkali and you want to get a body which will use 0.25%, how would you go about working out such a body?

T. A. SHEGOG: We would lower the ball clay content to the amount of electrolyte required, because it is on the plastic material of the clay that the electrolyte acts. We would reduce the ball clay.

C. C. TREISCHEL: Has any one found soda blisters in a cast like this and overcome them by a body change?

F. H. RIDDLE: Suppose we did not know anything about casting at all, like a man out of school who wanted to get a casting slip. If he did as he had been taught, he would probably get all of the clays that he knew of or could find out about which were clays that had been used successfully. He would try out each of those clays individually to see how they behaved with electrolytes. Then he would pick those clays which seemed to have the widest range where the effect of the electrolyte was as uniform as it could be; also, those clays which required the least amount of electrolyte to give the best results and work on those as a starter for his body.

Another thing he might also do is to study the literature and instead of doing the work himself find out what others have done.

E. SCHRAMM: I should like to say that Mr. Shegog's statement about the action of the electrolyte on the ball clays is not consistent with the work which we have done in the deflocculation and sedimentation of clays. The ball clays are characteristically dispersed as we get them whereas the English china clays are usually highly flocculated. It would be my belief that the action of the electrolyte to deflocculate the clay would be on the china clays rather than on the ball clays. I have had no direct practical experience with changing the ball clay content of casting slips. This is simply an opinion based on my understanding of the properties of the different clays.

K. M. SMITH: I think that can be easily shown. If you take plastic clay and dope it up it will usually get thicker. That goes to show that the ball clays and plastic clays are natural deflocculating agents. The higher you get a ball clay the less dope you need. It seems to me that the deflocculating reagent acts on the china clays and not so much on the ball clays.

T. A. SHEGOG: The question has been raised on what portion of the clay does the agent act. If we accept the colloidal theory that the electrolytes can act only on the colloidal matter in the clay, we must remember that china clays are very low in colloidal material. I have found figures like $^1/_2$ of 1% colloidal matter in English china clay and up to 5% in English ball clay.

It would naturally take more electrolyte to act on 5% of colloidal matter in English ball clay than it would on $^1/_2$ of 1% in the china clay.

W. K. MCAFEE: One of the ceramic engineers of a Trenton sanitary pottery has succeeded in reducing his electrolyte in a laboratory experiment to almost unheard-of limits by increasing the ball clay content in the body. That would seem to confirm Dr. Schramm's statement. I believe the solution would be to increase the ball clay rather than to decrease it.

R. W. HEMPHILL: We have two casting bodies. One is about 23% ball clay and takes 0.4 of 1%. We have another one with 16% or 18% of ball clay and that takes about four-fifths as much electrolyte which is just the opposite.

I. E. SPROAT: This difference of opinion seems to be due largely to the type of ball clay that they are using. A lot of our ball clays contain organic electrolytes. If we use a light colored ball clay with a small amount of organic material, ten chances to one it will take more electrolyte. On the other hand, if we use one containing a large percentage of these organic electrolytes it will take less.

C. C. Treischel: A little experience I have had along these lines seems to indicate that an increase in the ball clay, particularly of the types that we were using, for casting electrical insulators, reduced materially the amount of alkali necessary for deflocculating that particular slip.

We started out using about 12% ball clay, and with the same ball clays increasing to about 22% decreased the amount of alkali by about one-third. Then we changed the ball clays, and finally with the same 22% of ball clay content reduced the alkali to slightly less than one-half of what it was originally. It was slightly less than one-half, because originally we were using soda ash and sodium silicate on a half and half basis, and we used in the last body the same amount of soda as we used at the start and eliminated entirely the sodium silicate. Sodium silicate is regarded as a more active deflocculator than the sodium carbonate. That was with Tennessee and English ball clay. There was a change in the ball clay type used, showing that no doubt the organic salts carried by the clays played an important part.

T. A. Shegog: Do you not think in this discussion that we should confine ourselves to the same ball clay? If an increase in ball clay reduced the electrolyte required, would it not be logical to suppose that the time would come when we would either use no electrolyte at all or actually have to add a deflocculating agent, acetic acid or something else? I mean to say if the actions are inverse, would not the time come when by sufficiently increasing the ball clay we would not need an electrolyte at all?

D. W. Ross: Mr. Sproat, will you enlarge upon this idea of organic salts, what some one or more of them are; what their general nature is?

I. E. Sproat: If you can get an organic chemist to make an analysis of these clays and tell us what they contain, I would be satisfied. It is a difficult thing to say just what they contain.

F. H. Riddle: If you have a clay that acts as a deflocculating agent or saves us from using silicate of soda and sodium carbonate, in the end, are we any better off? Do these salts, which occur naturally, do less harm in a body than those which are added; in other words, is it an advantage to cut down on the additions of electrolyte?

R. E. Reif: We were bothered with soda blisters, but we are now making a slip without any soda at all, just with straight silicate, and have eliminated soda blisters altogether. We made this adjustment with our darker ball clays.

H. Goodwin: Are soda blisters due entirely to the action of the soda? I think we shall find it true that when the deflocculent becomes part of the body it will have some effect upon the question.

I. E. Sproat: The soda salts come to the surface and blister.

F. H. RIDDLE: Is there anything else that comes to the surface outside of these highly organic ball clays, if there is no soda that is not put in?

I. E. SPROAT: Organic acid very seldom comes to the surface. To a certain extent then it is an advantage not to have to use the salts.

C. C. TREISCHEL: That point was brought out by Mr. Sanborn somewhat in his paper, in which he told about the blistering trouble being eliminated by reduction in the use of alkali.[1]

Question 5 What troubles would one expect with an excessive amount of electrolyte in drain and in solid casting?

If we had a body that normally required 0.35% alkali, and through some change in the clays with which we were not familiar, we found that we had to increase the alkali content up to 5% in order to get the same results with regard to specific gravity and viscosity, what trouble would that cause in drain casting? Would it tend to hang, or not drain clean?

M. R. HORNUNG: That does not have so much to do with the amount of electrolyte as with the thickness of the slip. If the slip is thin enough it will drain pretty well regardless of the amount of electrolyte in it.

PAUL TEETOR: Slip requiring an excessive amount of electrolyte usually works satisfactorily if it is not too thick. Balling, however, may take place; that is, there seems to be a tendency for the slip to congeal after it has been poured into the mold. There will be little trouble with a piece which casts quickly, but with a piece requiring one and three-quarters to three hours to cast, the slip may sometimes thicken enough so that the slip becomes so viscous that the pressure can not force the slip into the more remote portions of the mold. This results in a tendency toward hollow casting, or in balling. Especially is this true if it occurs where a web branches off from a side wall. If it is completely deflocculated it drains very nicely. If it is not, there is some tendency to hang and not drain clean.

C. S. MADDOCK, JR.: When we first went into casting we used a solid cast of about $^5/_8$ to $^3/_4$ inch. When the men complained of the slip not working right, one of our foremen promiscuously added salts to suit himself, and to satisfy the workmen. When that ware came from the kiln, we found excessive blisters, or, after a period of 24 or 48 hours some of the ware would dunt. In one case they went up to 50% of dunted ware out of a kiln.

At this time we were experimenting with one-fire ware. We discovered that in the one-fire ware, where the glaze was put on the clay, that all the pieces made with clay having excess salt came out good. We put all the ware of the clay having excess salt through one fire without losing any of it.

F. H. RHEAD: The condition experienced by us in connection with an excessive salt content has been that we always had a deposit on the ware when it came from the bisque kiln. In addition to this, the molds developed a heavy film or crust, and for a period we had to scrub the molds after each casting. When we cut down the salt content, the deposit on the bisque ware and the film on the molds did not occur.

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[1] See pp. 555–64, *This Journal.*

C. C. TREISCHEL: In other words, you had more attack on the mold from an excessive amount of electrolyte and also on the ware itself. What was that coat on the ware? If you had broken the ware could you distinguish a difference in texture at the surface and in, we will say, up to $^{5}/_{1000}$ to $^{10}/_{1000}$? Was the texture the same?

F. H. RHEAD: The coat or film generally appeared on the upper surfaces that were exposed, both during the drying and firing periods. In the case of vases, the coat would be around the edge and on the top of the handles. If the vases were dried and fired up-side down, the coat would occur at the base, or in other words, at those surfaces that would dry first.

C. C. TREISCHEL: Could it be removed readily by sponging or scraping?

F. H. RHEAD: No. In most cases, the coat was not in evidence until after the bisque fire. The coat had a glossy blistered surface and was sometimes quite red in color.

C. C. TREISCHEL: Could you notice it in the green ware?

F. H. RHEAD: No.

T. A. SHEGOG: I had a case some time ago where cobalt sulphate was used for stain, and the accumulation of sulphate in the press water, which was used over and over again, became excessive. The foreman increased the amount of dope in his casting slip so as to decrease the viscosity. The slip was becoming thicker and thicker. We found that a state was reached when the surface of the ware, after the mold was drained, when exposed to the air actually dried faster than the surface in contact with the mold. When we used fresh water in our blungers the whole trouble disappeared. Whether this was due to an excessive amount or not, I am not prepared to say. I think likely it was.

D. W. ROSS: Part of a lot of ware affected similarly to that mentioned by Mr. Rhead, was fired with unsatisfactory results. By removing the surface coating with a soft dry brush the balance of the ware was reasonably satisfactory after firing.

C. C. TREISCHEL: You mean brushing it off from the green ware before firing?

D. W. ROSS: Yes.

A. S. WATTS: I saw a case similar to the one where they used the brush and they also sponged a lot of them. The sponge treatment did not seem to help at all; the salt worked into the surface on the dried ware. They did, however, correct the trouble by brushing.

H. GOODWIN: I had trouble of that sort. When biscuited the creams and sugars apparently took the glaze all right, but from the glost kiln they had scarcely any glaze on the portions which had scummed.

Question 6 What causes "balling" and how may it be overcome?[1]

Question 7 What causes "pinholing" and how may it be overcome?[2]

Question 8 What mesh feldspar (and other non-plastics) gives best results in casting?

C. C. TREISCHEL: How about the fineness of your non-plastic material? What effect does that have on casting? Does it speed it up or slow it down? Does it have any effect on the amount of alkali necessary for deflocculation?

T. W. BLACK: There is no doubt but that the size of grain of the materials in a body are going to affect the casting but in what way I am not prepared to say. I believe it is very important. We have a very coarse flint (20% will not go through a 100-mesh screen) and I found that it cast as well as the finer flint, but that it was the cause of crazing. Dr. Mellor, who visited our plant, told me that coarse flint was one of the principal causes of crazing in the English potteries and that they now had eight men who did nothing but test the flint for the English potteries.

I decided that the more variegated the grains the better body I would cast, of course within certain limits, but that the coarse-grained flint would certainly cause crazing. It did not seem to diffuse through the body as it should. The grinding of the feldspar used in the body does not seem so important as the fine grinding of the flint.

F. H. RHEAD: I do not see that the size of grains makes any difference if the body is properly adjusted. We have casting bodies that are as fine as they can possibly be, and we have others using material varying from 8- to 20-mesh, and they all cast equally well.

T. W. BLACK: I did not mean that it cast better. We had no difficulties with the casting of coarser materials.

W. K. MCAFEE: I had a little experience with this flint question. We are informed by the people from whom we purchased our flint that we use a finer flint than most of the sanitary potteries. However, we sent a sample of our flint over to Dr. Bernard Moore in England and he told us that he had had no experience with any flint that coarse and could not advise us.

T. W. BLACK: Dr. Moore has a very simple elutriator for flint.

K. M. SMITH: It is not difficult to cast with various sized grains, but it is when the ware goes through the kilns that it gets the real test.

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[1] W. K. McAfee, "Balling in Cast Ware," *Jour. Amer. Ceram. Soc.*, **8** [7], 430 (1925).

[2] R. W. Hemphill, "Observations on Pinholing in Cast Ware," *Jour. Amer. Ceram. Soc.*, **8** [3], 145–74 (1925).

C. C. Treischel: What effect does the fineness of grain have on dunting? Will the fine grain flint give a cast body with a greater tendency toward dunting than the coarser grain flint, or vice versa?

F. H. Rhead: I think this depends, first on the composition of the body and secondly, on the firing temperature. I recall an earthenware body biscuited at cone five that will dunt if 28% fine grain flint is used. But if the flint content is reduced about 5%, or the bisque temperature raised to cone 6, there will be no dunting.

I do not believe that the fineness of the grain alone, controls dunting or crazing. We make a variety of shapes and sizes with porcelain, stoneware, earthenware and terra cotta bodies. Certain porcelain slabs, approximately three feet long, twenty-two inches wide and a little more than one-fourth inch thick, are made with fine materials throughout. Such slabs will dunt if they are under-fired in the bisque and if allowed to cool too quickly.

C. C. Treischel: Single fire or double?

F. H. Rhead: Both.

F. H. Riddle: Were those vitreous, Mr. Rhead? Do you use setters for each as in terra cotta to fire them?

F. H. Rhead: The slabs are quite vitreous. They are made in a two-part mold and are cast on edge. After the slab has been cast, we remove one side of the mold and replace this with a refractory slab which exactly fits the other half of the mold. The whole business is then turned over, the remaining half plaster mold raised, leaving the porcelain slab on the refractory slab. The porcelain slab is not moved from the refractory slab until it is fired.

F. H. Riddle: How is it placed in the kiln?

F. H. Rhead: The refractory slab is placed flat on the top of the Harrop kiln. A handful of sand is poured on each corner of the porcelain slab.

Question 9

What are the possibilities of casting in rapidly revolving molds?

T. W. Black: My reason for asking that question was to find out if anything had been done. I understand that one pottery has been trying it out recently, casting plates and cups with handles on, but I also thought something might be suggested along the lines of drying molds by rapidly revolving them at a very high speed, about 1500 to 2500 revolutions a minute.

Some years ago in the Middle West a man was making cement vases and doing it by the dry process. They can be made very rapidly, but there is not a good crystallization of the cement. By using the wet process they have to stay a long while in the molds which necessitates a great many molds. This man had the idea of revolving them at 2000 revolutions a minute. He was able to put the cement in quite wet, a little thicker than our slip, and get them out in two minutes.

Another instance was a lumber company in the southern part of America. I understand that lumber takes considerable drying before it can be turned on a lathe. It takes some months, I believe. This man took lengths of timber cut from the woods, revolved them on a table in somewhat similar fashion and was able within a half hour after cutting the lumber to turn it on the lathe.

If principles involved in these two very dissimilar cases are sound, they are applicable to any industry. Because a certain principle has not been used before is no reason why it should not be tried out, and if there is any method of drying molds by any system like that it would cut down the cost of molds quite considerably.

This system has been patented recently. They have a mold rapidly revolving on an inclined plane. The slip is poured into the mold and after revolving a few seconds the mold can be tilted and the excess slip throwing itself out into a receptacle. I do not know how far they have gone or how successful it has been, but the one point I had in mind was that while science has made great strides in chemistry of pottery very little has been accomplished on the engineering side of the question with the exception of kilns. In the formation and the general shop practice, the engineer has not been consulted.

An engineer could come into the business without any traditionary bias, and I believe we might get some remarkable results. For instance, one pottery I have heard of since I have been here, prepares the slip by passing it through a vacuum. They are also mixing their clays a little differently. They have a re-mix that comes from the pug mill. By eliminating the causes of unequal shrinkage of bodies during the drying and firing it would make the production of china ware or vitreous ware as simple as the making of semi-vitreous ware because it is the air in the body which causes deformation more than anything else. If the air voids in a body were eliminated or decreased or uniformly distributed through the mass, unequal shrinkage during the firing of the ware would be minimized, total vitrification would occur, quicker and more evenly. This seems to me a line of research for the engineer rather than the ceramist.

F. V. DRAKE: In answering part of the question of the previous speaker in reference to the engineering in potteries, it has been my experience that every time the engineer takes up a subject of that kind the potter refuses to coöperate. He wants the engineer to experiment until the thing is perfect, then possibly he will adopt it.

F. H. RHEAD: We worked out an experiment some time ago in regard to revolving molds. We were casting porcelain bowls, from sixteen to eighteen inches in diameter, in the ordinary open molds. As we were having warping troubles, we put these molds in a jigger and sprayed the slip while the molds were revolving fairly rapidly. We made a number of pieces, none of which were over one sixteenth of an inch in thickness. There was practically no warping and the thickness was as uniform as a cast piece. As a sprayed surface sometimes develops a wooly texture, especially if the mold is too dry, we use a potter's rubber to finish the inside of the bowls.

E. SCHRAMM: Do I understand that you used no excess slip in that process but just sprayed in enough to make the form?

F. H. RHEAD: We sprayed in enough slip to build a coat of the required thickness.

E. SCHRAMM: Did you try drain-casting in connection with the revolving mold?

F. H. RHEAD: No.

R. W. HEMPHILL: I do not see why somebody does not get up a continuous filter press of some sort. Pump the liquid into the machine and have it come out in the shape of pugged clay. I think it could be worked out.

C. C. TREISCHEL: The man who is mining clay for use in the rubber mills described a process that might be applied here. (Spray drying as in the manufacture of powdered coffee.)

R. W. HEMPHILL: But that dried it too much.

Question 10 Can American ball clays and china clays be used in casting bodies?

T. A. SHEGOG: There is no doubt but that American ball clays and china clays can be used in casting bodies. We have been doing it for a couple of years.

C. C. TREISCHEL: This can be easily accomplished if necessary precautions are taken to accommodate the idiosyncrasies of the American clays as compared with the English clays.

If the whiteware industry in this country had been built up on the basis of American clays and we had tried to substitute English clays for them you would have had about the same problems as you sometimes have when you are doing the other thing.

T. A. SHEGOG: There would be exactly the same difficulties. We cannot transplant a process, but we can adapt it. There is not any great difficulty in that.

Question 11 What kinds of clays give the best results in casting bodies?

R. W. HEMPHILL: Do you consider talc clays in a thing like that?

C. C. TREISCHEL: Hardly.

R. W. HEMPHILL: Is cast talc body all right?

D. W. ROSS: Some years ago Mr. Cermak told me that the dark ball clays were the ones that would cast and dry most satisfactorily. On casting bodies containing the dark clays, a darker area is frequently found near the surface of the dried ware. It would seem from this that some of the organic materials, whatever they are, do actually travel to the surface and must be more or less soluble. What is the real opinion concerning the relative ease of casting dark and light clays?

R. E. REIF: Casting can be done as well with the light clay as with the dark, providing the alkali is adjusted. We have used practically altogether a white ball clay. If we use 1% silicate it casts just as well.

C. C. TREISCHEL: Is there anyone who has anything to say regarding the routine testing of clays for use in casting bodies? Are the clays which are used in the casting body tested in a different way than the same clays that are used in the plastic process, for instance? That question has been asked by Mr. McAfee. He is seeking information.

F. H. RIDDLE: If English china clays are used in the body and their behavior is tested with a definite amount of electrolyte, or if those clays are put into a slip with a definite amount of water so that the specific gravity is known, and then the electrolyte is varied and the viscosities are determined, the variation in one car from another can be found. If you have not done that before that may explain some of the reasons why you have variation in the casting slip from time to time.

I know of two or three instances where the selection of the china clay has caused a whole lot more trouble than the selection of ball clay. We have talked as though the ball clay were the principal place to find trouble, but I think you will find just as much or more, particularly in the heavy casting, in the china clay than you do in the ball clay.

C. C. TREISCHEL: It would hardly seem natural that an entirely different process from the plastic in which we utilize so much of the most minute particles in the clay substance would give a great deal of information or enough information to act as a guide for the casting process.

The Standards Committee have done nothing regarding the testing of materials for casting process, but as this process is getting to be such a big factor in the forming of whiteware in this country it seems as though we have some work ahead of us in the devising of standard tests for clays for use in casting.

C. C. ENGLE: Mr. Riddle, what would you suggest as a standard for use for comparing one clay with another, what amounts and what materials, to adopt as a standard of comparison for a lot of different clays, for example?

F. H. RIDDLE: Without having had an opportunity to give it any serious thought what I think I would do would be this: Keep a certain amount of the materials that we know the exact content of and which have worked satisfactorily; make up a small amount of body from those materials with the exception of one of them which would be a new supply. For instance, if we wanted to test out the ball clay, we could make up the new body with flint and feldspar and china clays; then put in the new shipment of ball clay and test it out with a known specific gravity, varying the electrolytes and plot the curve for the viscosity. That would give an idea of the behavior of that particular clay and how it affected the body as a whole. If we find the curve running right along normally we feel pretty safe in casting with it.

C. C. ENGLE: I had more in mind this matter of testing the clay for its properties.

F. H. RIDDLE: The reason I brought it up that way is that the average man is interested in, not the clay by itself, but what it is going to do to the body, and that process would give that information. Some similar procedure would be used to test the clay by itself.

In our laboratory we have so calibrated the little mills as to grinding performance that we can in the small mill produce a body which can be duplicated in the six foot mill. It took a long time to determine the grinding schedule which would produce like results in both mills.

I realize that in the heavy clay ware where we are using car after car and the material comes in and is dumped into the bin that it is very difficult to do anything except to talk the thing over after it has happened. But by testing the clay occasionally, even if that clay has gone on into the bin, and a variation in the ware found, it pays to check back to determine the cause of variation. It pays to separate the clays more carefully or to hold them back until they are tested if this trouble is found too often. From time to time it is found that a clay will gradually change so that in a few carloads an entirely different amount of salts is being used from the amount used three or four months before.

E. H. FRITZ: We have not been able to devise a test for properties of clays which is satisfactory; that is, for casting, of course. We are working on that, however.

At the present time we are doing just as Mr. Riddle suggests. We introduce the clay that we want to test into our standard body, keeping all other things the same and then come to our viscosity limits such as we described in our paper[1] and cast with that a piece which is most sensitive to variations. That always is a piece with a very heavy section.

It is not necessary, however, to use a standard design. Any standard test piece can be used. But a test of this kind is the only test as far as I know that really shows the variation in the clays.

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[1] E. H. Fritz, "Some Observations in the Casting of Heavy Electrical Porcelains." *This Journal*, pp. 547–54.

K. M. Smith: If you do find something the matter, how are you going to fix it? Let us take an English china clay. Suppose we find it is off. Are we going to correct it by adding more flint? Suppose that it is cracking too much. Are we going to correct that by adding an inert substance like flint or something else?

F. H. Riddle: We know where to start and that is worth a great deal. It is good practice to use clays of several sources so if one goes wrong it does not have such a serious effect on the entire body.

E. H. Fritz: Since we established our present casting control such as we described, we have not had any trouble whatever due to the casting behavior of the slip with ware less than four inches thick. We are only affected on the pieces heavier than that by variation in the clay.

A. S. Watts: We want to begin to consider diagnosis very seriously. If people will do just as Mr. Fritz and Mr. Riddle have suggested, if they will diagnose the case carefully and find out where the fault is, then we can begin to take up the individual problems of how to treat the disease. I do not believe we shall get anywhere by the customary factory practice of saying, "Well, we changed kiln burners; that is the trouble; it is all on the kiln," or, "We have a new man in the slip house; there is the whole trouble; it was in the slip house." The result is that somebody else takes a mental vacation in the plant and as long as there is a new man in, he carries the load.

T. A. Shegog: In the general ware industry I think we are up against a condition which apparently we cannot very well alter. We have to use the same body for casting as for jiggering so that the body is at best a compromise. Very few of our plants are equipped to run with two different bodies. Very often we may know where the trouble lies but we can only ameliorate the condition; we cannot get out of it.

Question 12 What faults are caused by an increase in specific gravity of a slip? By an increase in viscosity? By a decrease in each case?

F. H. Riddle: Specific gravity and viscosity are supposed to be the very interesting properties of the slip. They are heart of the subject.

C. C. Treischel: What will happen to the casting body in the factory if suddenly the weight of the slip goes up? What trouble is there? Is there balling, soft centers or cracking in the molds?

Many times it is good practice to know about these things before they happen, so if we get the slip that way we can expect trouble to come. I do not suppose any of us have slip that varies that way. Maybe it goes the other way. What will happen if it goes down? If we are running 32 ounces to the pint, suppose it goes down to 31 ounces, $30^1/_2$ ounces? What happens?

W. L. SAMPLE: We had a peculiar experience recently. We get the specific gravity of our slip by measuring in a bottle. Somebody switched bottles on us, the specific gravity went up, the weight per pint went up an ounce and a quarter and the slip got rather thick and would not drain very well. It was not as good as our regular slip. It did not make much difference apart from the slowness of draining. We do not take much stock in the specific gravity or viscosity reading. We have a viscosimeter but it is rarely used.

They have been making slip at our plant at Newcastle for more than ten years and they never bother about the viscosity determinations. They just pour a little slip in the mold and cast with it. The results are quite satisfactory. But to come back to the question: increasing the specific gravity *per se* makes the slip so that it does not drain well. A definite viscosity reading has nothing to do with the way the slip will cast. The way the slip will cast will have something to do with the viscosity, but I have not been able to get any check on it. Viscosity is one thing one day and another thing another day. I do not care about the viscosity except incidentally.

C. B. YOUMANS: We find that the weight does not vary a great deal, but we do find that the viscosity will vary, and if it does it will give us trouble. Our tank men like a very much more viscous slip than the wash down men. We have only the one to supply both men. We do not have to vary the weight at all; apparently, it does not seem to make much difference. The viscosity gives us a great deal of trouble. We are more interested in viscosity than in specific gravity.

K. M. SMITH: I ran some tests on viscosity and found a variation of 15 to 20 seconds, which I thought was very bad. That was for 100 cc. After hearing some of the discussions that were brought out yesterday where one man allowed two minutes, I do not believe ours is very far off. It will not vary more than 25 seconds, so I think one reason why we are not having any trouble as far as viscosity is concerned is because it stays within that limit.

C. B. YOUMANS: Ours is 200 cc. That will make a difference. You only have a hundred.

K. M. SMITH: We could use 200 cc.

C. B. YOUMANS: You will find it different there.

E. SCHRAMM: What is the size of the outlet?

C. B. YOUMANS: It is the standard size.

E. SCHRAMM: The ordinary viscosity test is one in which a can of some kind is used and the slip is allowed to run out. We find it more convenient not to let the slip drain completely, but simply to run into a graduated cylinder a volume considerably less than the capacity of the can, so that the test is not complicated by the extremely slow delivery towards the end.

F. H. RIDDLE: It might be of interest to know that we have a Bureau of Standards viscosimeter made of copper. We made a good many tests, particularly on glaze. We made one out of aluminum so that it would be lighter for the girl to handle. The difference was very marked between the speed in the copper and aluminum viscosimeters. When we talk about viscosimeters we are talking about wide variables.

W. K. MCAFEE: Much of this apparent dissention on viscosity, and differences in specific gravity, depends on the skill of the men using the slip. Experienced casters can handle a thick slip one day and a thin slip the next. In other words, they carry a pretty good viscosimeter in their fingers. They can tell by the "feel" of the slip.

An increase in specific gravity will slow up the draining and in some of the complicated pieces may cause hanging and trouble of that sort. A decrease will possibly give more trouble than an increase due to excessive shrinking.

C. C. TREISCHEL: There are many different things that are used to test viscosity—all the way from sticking our hands in the slip up to machines that cost $200 to $300. We shall never reach a conclusion if we talk viscosimeters. No matter what type we use we can get a working curve showing the viscosity of the particular body that we are using. The curve which was shown on the sheet yesterday in the slide by Mr. Sanborn is something of that sort. Suppose we are working in the range, *a–b* (Fig. 1) that is our limit. What will happen if the slip does not flow as fast? Suppose we are above *a*. What will happen to the slip? That is what we want to get at in this question. What will happen if we get down below *b*? We know that settling will occur if we get below *b*. We get thickening above *a*. I do not know what trouble that will cause in casting. A slip will thicken on standing and thicken rapidly if it is near the range *a–b*. If the workable range on a body runs from *a* to *b* it will cast faster at *b* than at *a*. I know one man who uses that for control. He has a body which if deflocculated in the ordinary way would cast so fast that his men could not keep up with it. So instead of varying his clay for control he controls it by alkali and stays near *a*. He has a very thick slip which is viscous but not heavy. It does not flow well. Can someone tell us what would happen in casting, if we get up above *a*?

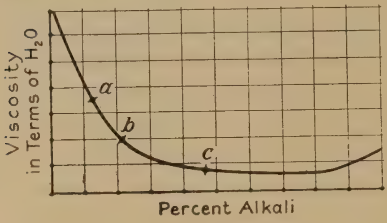

FIG. 1.—Casting discussions.

P. SANBORN: If we get up above the second line, the ware when it is cast will act quickly, but when we take the ware out of the mold or take the mold away from the ware, (sanitary ware) it is not solid. The ware will have a tendency to settle down, that is, if accidently bumped it will tend to warp without cracking. The pan of a bowl will settle and if propped up it will dry perfectly straight. When it comes to the inspectors they will not see anything the matter with it. The only trouble is that invariably when it comes from the kiln it will be warped just precisely as it was warped in the green stage.

K. M. SMITH: Do you find when you get over to the right side of the curve that it is over-doping the slip? If the cast, taken between your fingers, is brittle and hard when squeezed or pressed together it will cause cracking in drying before you can get the molds away from it. While if you stay on the left hand side of the curve (if you get high on the curve) your ware is jelly-like. It is very soft and quite plastic when pressed in the hand. I do not know whether that is due to the sodium carbonate or silicate. The general opinion is that the hard feeling body is due more to the sodium carbonate than to the silicate.

C. C. TREISCHEL: It seems to me that comes from a question of the difference between clays which are flocculated and those which are deflocculated. At the right of *c* you have a flocculated condition which is entirely different than where it is deflocculated left of *c*. The material in the clay is in an entirely different state.

Question 13 How can we account for differences in viscosity from time to time at maximum deflocculation and constant specific gravity?

C. C. TREISCHEL: Suppose this is the curve (see Fig. 1) of a body that is worked at 32 ounces to the pint, and we are working in the range *a–b;* and to get a flow corresponding to 32 ounces to the pint, we should have to add considerably more alkali.

It would seem that we have not in any way changed the clay content of the body because the specific gravity of the casting slip depends entirely upon the amount of clay and inert materials and water. If that is constant we have every reason to believe that these conditions are constant. Still, it takes more alkali to give the same rate of flow. That is the question as it was explained to me by the man who proposed it.

Will variation in temperature cause that? It is a thing that is likely to happen more in the winter than in the summer, especially on Monday mornings after the casting shop has cooled down over Sunday. What other things would cause it? Will the variation in the ball clay cause it? If so, why? Will the variation in the size of the grain of the flint cause it, or feldspar?

W. K. MCAFEE: I believe it is a practice in some of the European plants to actually age the slip after it is made. That is more or less allied with this question. I wonder if anybody in this country is trying that?

K. M. Smith: It was brought up in Mr. Sanborn's paper that after aging four days the viscosity was lowered appreciably without any changes being made in the actual content of the slip.

C. C. Treischel: That was in connection with a different sort of deflocculating material than most of us are accustomed to using. The material he was using for deflocculation was much slower in its action than soda ash and water glass.

K. M. Smith: From the discussion of Mr. Sanborn's paper it developed that the organic deflocculating agents came from the ball clay. Four days of aging seemed to be the maximum time the slip lowered in viscosity and yet stayed constant in weight. After the four days the viscosity did not decrease any more. He explained that as being due to the organic deflocculating constituents from the ball clay.

C. C. Treischel: I am afraid that you misunderstood part of Mr. Sanborn's statement. What I brought out from him was this: if at *a* on the curve, as the slip ages it comes down to *b* and he then casts it, this, *a*, was 125 seconds flow and *b* was around 108. Point *a* is the place where the slip comes from the ball mills and goes into the aging tanks. It then is allowed to age down to *b*, when it will run steady. On further aging it will start to thicken. That means that it comes down to a point where he gets the maximum effect from the deflocculating material and then the slip starts to thicken up due to adsorption of this deflocculating material.

Mr. Sanborn did not say that he uses soda ash or sodium silicate as his deflocculent. He said that he determines whether he is on the right or left of *c* by adding sodium silicate to his slip to test it. If it gets thicker he knows that he is on the right side, if it gets thinner he is on the left of point *c*.

Question 14

Do all body mixtures have the same relation between specific gravity and viscosity to produce best results in casting?

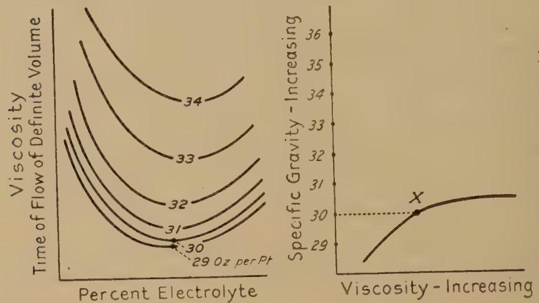

Fig. 2.

W. K. McAfee: This is rather a deep question to answer offhand this way and I should suggest that some of us obligate ourselves to take the bodies, make this curve as you suggest there, and send them to a clearing house to see how near alike those curves are; whether or not they do follow the same form. They might then be referred back to each of us to see what results we could get with specific gravity determined in that way.

I do not think that we can answer it here, but we can make plans to answer it in our own plants.

Question 15 On what property of a casting slip have we the greater percentage limit in variation, specific gravity or viscosity?

C. C. Treischel: This question has been answered above.

Question 16 What causes the formation of a definite skin of fine clay on the surface of a cast piece? This skin fires a darker color and is extremely vitreous.

That question came all the way across the Atlantic Ocean. If any one has anything that will answer it I know our friend over in England would be glad to hear what we think about it in this country.

C. B. Youmans: We would say it was too much soda.

A Member: The clay will go to the surface. If we have a surface of clay it will naturally vitrify a little but quicker than the center of the body. We experimented on heavy clay products. The other day we used a little sawdust. This was in the center and we had a hollow piece when we got through with it. The sawdust burnt out and showed practically all clay on the outside.

H. Goodwin: It is affected by the way the caster fills his mold. There is an alkaline content which comes to the surface which affects that skin there.

T. A. Shegog: Are you referring to the brown stain that forms where the slip drops in the mold?

H. Goodwin: I have had about 17 explanations of them but none of them have been very convincing.

C. C. Treischel: Mr. Shank of Shank and Company, Ltd. has asked this question. He refers to that idea of the slip striking the mold, but that does not seem to be where his trouble is. He states, "We have sometimes been troubled with scumming or rather the formation of a definite skin of fine clay on the surface of the cast piece. This fires a darker color and is extremely vitreous. We have the same phenomenon where the slip first strikes the mold, occasionally spreading to a considerable area and accompanied by blue stains. These are fairly common in cast ware, and, of course, show up very much more in the case of a vitrified piece."

T. A. Shegog: The phenomenon is perfectly common, and although I would not like to venture an explanation as to what is the cause of it, it has been discussed for many years. I can tell him how to stop it, if that is of any assistance.

It usually forms about as big as the palm of the hand, perhaps about the size of a half dollar, just where the slip strikes. If the slip does not strike it will not form, so I have stopped it within the last couple of years by letting the slip fall on a brass plate mounted on three little legs, so that it strikes the brass and spreads out. In sanitary ware you can stop it by having a bent tube and pouring through the bent tube, with a funnel, so that the slip rises in the mold instead of striking the bottom in falling. Either way will stop it, but I cannot tell you the cause of it.

W. K. McAfee: Not only the striking in the bottom of the mold will give a streak, but an appreciable striking of slip against the mold after the slip is actually in the mold and the mold is pretty well filled up, also gives a streak. I did not understand that that was the problem in this question, but I am glad that it is because I never have heard any explanation of that streak, either. The only way that I know of to prevent it is to keep the slip from the side of the mold as long as possible, *i. e.*, to have it rise uniformly from the bottom.

C. C. Treischel: Filling the molds from the bottom will remedy it.

W. K. McAfee: In casting closet bowls we fill the mold from the bottom. In going to the bottom the slip has to pass through a small hole in the trap. Of course, we are using the overcast method where the trap is cast the day before and we pour the slip over this trap. The trap has a small hole in the bottom and if the caster pours the mold too fast the slip will overflow the trap and strike the side of the mold. Invariably we get a brown streak which burns blue where that slip runs over the side of the trap. We provided the casters with pouring troughs with an orifice of a fairly accurate size so that it is impossible to pour too fast.

Question 17 What are some simple, reliable and rapid methods for measuring viscosity of thick and heavy slips?

C. C. Treischel: This question also comes from abroad. Evidently what the gentleman had in mind is the measurement of the viscosity of slips which are too thick either from being too viscous or of too high a specific gravity to flow through viscosimeters of the ordinary flow type where we stay below a quarter of an inch orifice. Has any one had any experience with the tortional type of viscosimeters? Has any one used a viscosimeter with an orifice of half an inch or more, holding a gallon? I know Mr. Bowman has.

W. J. J. Bowman: Our method is not a very close measurement. We use a U-tube, $^1/_2$ inch in diameter with a funnel attached to either end of the U-tube. We fill the one funnel with a given quantity of slip and take the time required to rise to a given height in the other funnel. We have found when we weigh a pint of slip and make slight addition of water to the blunger we could not detect (by weighing another pint of slip) any change in weight, but there would be a change in the reading of the viscosimeter.

C. C. Treischel: Does the instrument work all right for the body for which it is devised?

W. J. J. Bowman: We have been using it for years. We know that when the slip rises in the funnel of the viscosimeter to its level in a given time it will work in the mold all right.

C. C. Treischel: One man asked me if anyone had had any experience with viscosimeters for use on casting of grog ware, such as the fire clay sanitary ware, sometimes called solid porcelains. What do they use in that industry?

W. J. J. Bowman: That is what we use it for.

Question 18

Why is it that two mixtures will give slips that apparently cast and work the same, yet one will be full of "pin holes" and the other perfect?

C. C. Treischel: This question has been asked by a man who has given us a large amount of information on pinholing. It ought to be a good idea to reciprocate.

Will the rate of flow have anything to do with that? The slip that is fluid certainly should allow the air to escape from it more readily than one that is thick and viscous.

H. Goodwin: Have you seen that interesting discussion which took place in the English Ceramic Society on "Pinholing?" A short abstract follows:

In the course of his paper, Mr. Plant outlined numerous possible causes for this aggravating fault, which revealed itself in pottery production with such disastrous results, financially and otherwise, to the manufacturer. One local pottery manufacturer had estimated that his loss, through this cause alone, amounted to no less than two thousand pounds in a period of about twelve months, while every manufacturer encountered the fault in a greater or lesser degree.

The Causes of Pinholes

A case was cited of one manufacturer who was making a very fine line of under-glaze hand-painted pottery. A special palette of colors had been prepared and business was booming, the results, from a productive point of view, being excellent. But, all of a sudden, pin holes developed on the surface of the finished ware. This resulted in a very large percentage of seconds, 30%, at least, of the goods coming from the ovens faulty. All sorts of investigations were made with a view to putting a stop to the trouble. Special precautions were taken in the sliphouse; the glaze was brought under suspicion; experiments were made with other glazes; and then experiments with other colors; but although some improvement was made by fluxing of the colors, the loss still continued, until it became almost impossible for the works to deal with the orders on hand. Meanwhile, months had passed in this effort to trace the cause of the trouble, and, as so often happened, the remedy was the simplest possible. Instructions were given that the biscuit ware before being decorated, should be washed in clean water. Immediately, the pin holes disappeared, and up to date there had been no further trouble in this direction.

But there were numerous causes which led up to pinholed ware, and these the essayist proceeded to deal with individually, summarizing them as follows: Imperfect preparation of materials or clay; imperfect blunging; insufficient aging; faulty pumps, pumping air instead of clay; bad pugging; unsatisfactory press cloths; dust on the molds; perished molds; too much water used by the potter; cast mold being too wet; too dry or too hot; bad firing; and faulty glaze mixing.

E. H. FRITZ: Do you mean by pinholing the imperfection on the glaze surface only?

C. C. TREISCHEL: I think that is what they refer to.

E. H. FRITZ: That is not the term we use. I might be able to give something that might help you.

Our product, of course, is a one-fire proposition. We have found that we could not do any sponging on the ware without getting into this pinholing. We finally had to adopt the following procedure.

We blow the ware using an air pressure of about 40 pounds, removing all dust in that way, and then we spray the glaze on, but not necessarily the whole coat. We usually dip the piece of ware after it has been sprayed. By spraying we get the glaze into pits and crevices which have been uncovered by the air and were filled with dust. These pits are usually due to air in the slip.

The air, therefore, serves not only to remove all dust on the surface of the ware, which is very essential, but also to uncover the pits and crevices which are always present and are filled with dust. If we only sponge, we leave the dust in these pits and later glaze over it which will inevitably cause a pinhole. So I think we have found the answer in our cast ware at least.

W. K. MCAFEE: I think this whole question of pinholing is probably complicated by the fact that we are trying to include too many different faults under the term of pinholing. Some pinholing comes from air. I have seen strong evidence of what is apparently pinholing due to the glaze. Probably they are two different faults that look alike. There may be some more faults, which we call pinholes. Some of them may be due to shrinkage on a green piece and may not be air at all.

T. W. BLACK: I had some trouble with pinholing that occurred in the decorating kiln. We had no trouble with pinholing after it came out of the glost kiln but after it was decorated it developed. How do you account for that?

H. GOODWIN: This result could be obtained by too great a temperature in a decorating kiln, in comparison with that of a glost kiln and not be termed spit-out.

EDITOR: Pinholing in decorating kiln often is due to carbon particles which were covered, the ware not being cleaned.

Question 19 What are the possibilities of the casting process in the manufacture of saggers?

C. C. Treischel: Mr. Morris, could you tell us what the possibilities are?

G. D. Morris: I think that we are getting considerably better saggers today.

Two years ago we made up some cast saggers for a company using a Dressler kiln. They still have the same saggers with about 10% loss. I think Mr. McAfee can give you some information because they are making cast saggers and have been using them right along. Of course, we are making a large number of large slabs, and in comparing them with the pressed slabs, we find that they have a life in the tunnel kiln of about three times as long.

W. K. McAfee: I do not have any exact figures, but we get a considerably longer life out of cast saggers than we do out of hand or machine made saggers. We try to place cast saggers at the bottom of the bungs to build from. They remain much straighter and make a better foundation, are stronger and we feel a little bit more safe in starting the bungs off.

We subject saggers to about the same conditions as everybody else. We have not done a great deal of work on this. Apparently, a small percentage of carborundum in the cast sagger mix will further increase the life of the saggers. We probably do not put enough in to increase their conductivity but apparently this makes them a little bit stronger. The behavior of the mixture in the casting, as suggested a while ago, is advantageous. You have a mixture of clay slip and grog, with the grog in various degrees of fineness. The clay mixture will go to the outside and form a sort of skin. The grog particles will arrange themselves more or less with the finer particles toward the outside and the heavier particles in the middle. That gives a very nice structural shape. It comes automatically.

F. S. Crumley: Mr. McAfee, do you use the same mix for casting saggers as you do ordinarily?

W. K. McAfee: No.

W. J. J. Bowman: I have not had experience with saggers but for a muffle kiln. We had a better shape rather than a more refractory piece in our case.

W. K. McAfee: We found that a small percentage of the native red clay down near our plant will materially increase the mechanical strength of the sagger which, of course, is an advantage because that is where a lot of the sagger loss comes, handling them while they are out of the kiln. We find by adding a small percentage of that red surface clay that we get a tougher sagger which does not break so easily mechanically.

R. E. Elliott: I visited a plant where they kept the slip quite warm, which was a new thing to me. What is the point in having the slip heated?

G. D. Morris: You do not want to use warm water. It is all right to keep the slip at a warm temperature, but if boiling water is used and that goes into the mix there will be trouble. It is all right to keep it lukewarm.

C. C. Treischel: Two men who have had considerable experience in casting have told me that that is the best way. They passed live steam into the tank of water. It was stated that the water was almost to the boiling point when the clay was added and allowed to stand overnight, just soaking with the salts, and then stirred up in the morning.

G. D. Morris: You will have to dissolve the soda in hot water. It would work much better to do it that way.

Question 20 Are there any deflocculating agents in practical use other than water glass and soda ash?

Chairman Treischel: There are two materials of an organic nature which have been used to my knowledge. One is gallic acid and the other is extract of tannin. Has anyone here had experience with those materials? It was mentioned last year at the meeting at Atlantic City by one of the men from the Bureau of Standards that they were experimenting at that time with the use of gallic acid in connection with deflocculating a grog body for casting glass pots.

C. B. Youmans: We tried a little of that. It is very active much more than the salts.

K. M. Smith: It seems if something of that kind could be used we could get away from this skin that we are talking about on cast ware and would help our glazing trouble. It will give us a better bond between the biscuit and the green glaze before it goes into the kiln. I think it is well worth investigating.

Mr. Sanborn has used a considerable number of those organic materials in an attempt to find out an organic material which will act the same as the material which he is using from that ball clay he referred to. He has tried tannin and a lot of tannery extracts.

C. S. Maddock, Jr.: Gallic acid will produce a skin that is very hard.

E. H. Fritz: Has it ever been found out just whether this skin that forms from the use of the common deflocculents, especially water glass is not dependent upon the amount that is used in the body? We never encounter that, but our amount, I imagine, is rather small as compared to that used by others. Ours runs around .2 or .1%.

C. C. Treischel: On the basis of the materials as received or based on the Na_2O content?

E. H. Fritz: The per cent of water glass added is .2% of the entire mixture. It seems to me that the fact that we do not encounter this trouble must be due to using such a low amount. If that is the case, the answer is to develop the body in which higher amounts are not required.

Question 21 In connection with water glass, what ratio of Na_2O to SiO_2 gives best results? Will this vary according to the types of clay used?

C. C. TREISCHEL: Mr. Rhead asked this question. Has anyone had any experience with changing the water glass that they use from one specific gravity to another? How does that affect the slip?

C. B. YOUMANS: We had that experience. We use silicate of soda for our sagger cement also, using the U-brand for casting and the N-brand for making sagger cement. Due to a slip-up we got hold of the N-brand used for making the sagger cement and used it for the regular casting slip. The minute that happened our slip was thrown completely off. We find the U-brand is much better to use than the other.

C. C. TREISCHEL: When this mistake was made, how did it affect the slip? Did it become thicker or thinner?

C. B. YOUMANS: It was thicker. The N-brand did not have the deflocculating properties that the U-brand had.

C. C. TREISCHEL: Is the U-brand thinner or thicker than the other?

C. B. YOUMANS: Thicker.

W. K. MCAFEE: If we adjust the different brands for the actual specific gravity and vary the quantity according to the specific gravity, they will work about the same.

C. C. TREISCHEL: There seems to be a great deal of difference of opinion on the effect of some of these things, as I have talked to men around the country. One man will use soda ash, another man will use salsoda. He will say it is better in a hundred ways than soda ash, while it is nothing but soda ash with but ten molecules of water tacked on to it. He says it is better for deflocculating material.

Is it just a matter of opinion? Some one will use soda ash and get along satisfactorily and somebody else will use sodium silicate and get along all right. Another man in another part of the country will probably use salsoda mixed with water glass, half and half, and he gets along all right. Is it a question of having the right deflocculating material for the type of body or just a matter of opinion?

R. E. REIF: If I recall correctly, over in Germany there are some potters using nothing but soda for deflocculating agent, using it as sodium oxide, so it must be due to the water content.

D. R. KELLOGG: In comparing these various deflocculating agents are they all figured back to the same hydrogen-ion concentration? It seems to me as a chemist that is the secret of the whole thing. Some work done at our laboratory seemed to indicate that the hydrogen-ion concentration was an important thing. I have been wondering if these stories as to various brands of soda ash and salsoda, etc., have ever been compared on the basis of the actual hydrogen-ion concentration.

E. H. FRITZ: We have never actually determined that, Mr. Kellogg, but from my observation it is absolutely correct. It is entirely a function of the hydrogen-ion concentration.

When we first started to cast we used sodium silicate and sodium carbonate. After a while we decided that if possible it would be nice to eliminate one of them, especially the carbonate because the silicate is so much easier to handle in the liquid state. We did that maintaining the same Na content and we could not see any difference in the results.

E. SCHRAMM: I think there is no doubt that the question of the hydrogen-ion concentration is the important thing to be considered with any one deflocculating agent but sodium silicate has a much stronger deflocculating action in equivalent proportions than carbonate.

Our practice is to use sodium carbonate for the greater part of the deflocculating agent and sodium silicate as a control because of its extremely powerful action in small quantities. We vary the proportion of alkali from time to time and control our slip in that way. In other words, we use the silicate to take care of the variation in our conditions.

K. M. SMITH: Is it not the function of the sodium carbonate as a deflocculent to act as a hardener for the cast ware?

That seems to be the prevailing idea among the old potters and the men that have been in the plant where I am. They seem to think that if we do not have the sodium carbonate in there the ware will remain soft. The sodium carbonate hardens the cast ware so that the molds can be taken apart.

C. C. TREISCHEL: You mean that you can cast faster?

K. M. SMITH: Not so much in casting speed but in hardening the ware after it is cast, so that the molds can be removed sooner without the body remaining jelly-like.

T. A. SHEGOG: I found the sodium carbonate used in another way. Once in a while the cast piece showed a marked tendency to stick to the mold and it is difficult to remove. In those cases I have found that if we substitute a certain proportion of carbonate for the silicate we get over that sticking. That is particularly noticeable in casting handles. Sometimes they will not come out of the mold readily, and then each individual handle breaks off, but if we replace a certain proportion of the silicate with carbonate it does not stick to the mold nearly so much.

H. GOODWIN: I quite agree with Mr. Shegog.

PAUL TEETOR: Much depends upon the properties of each combination of clays. In some cases the ratio of sodium carbonate to sodium silicate can be varied over a wide range while in others it cannot. I have in mind a combination of clays which when made into casting slip with sodium carbonate in excess of sodium silicate will cast satisfactorily but the piece will not harden sufficiently so it can be removed from the mold the following day; in fact a little jarring will cause the piece to collapse and form slip again. If this same body is made into slip with the silicate predominating it will cast and harden as desired.

It is not always just a case of adding the proper amount of either of the salts but in some cases the properties of the materials have to be considered and the ratio of the two salts adjusted accordingly.

Question 22 What practical method could be adopted to test each batch of casting slip before it is put into use?

C. C. Treischel: Has any one used that system or process? Some of the men here use it because they have so stated.

W. L. Sample: We always pour a little slip in a mold and test it. It does not take very long. We are up against it for time. We have to make slip as fast as we can, and when the slip is blunged sufficiently we start to let it out and make a test at the same time, and if necessary we add more deflocculent while the blunger is being let out. I heard the remark made yesterday by someone that they did not have time to test each batch of slip. I do not find that it takes long.

Question 23 To what extent are casting problems concerned with the type or quality of plaster used in making molds?

C. C. Treischel Does the type or quality of the plaster we use in the molds make any difference in the result obtained? For instance, in sanitary ware casting do any of us use the same plaster that you use in the terra cotta industry?

E. H. Fritz: We had a rather interesting experience a few weeks ago. We found that we could use a greater ratio of plaster to water in making molds, which is desirable in the plastic process where the molds are given very rough usage. Unfortunately, we did not take into consideration what effect that would have in the casting molds and naturally the molds were made up the same way from the heavier percentage of plaster. After we put them into use we noticed that we were getting a considerable amount of pits or pinholes in the pieces after they were cast. We finally found that this was due to air actually coming out of the plaster. It seems that the air instead of going out of the plaster at the top of the core as it had been doing, crept out through the side of the core into the slip and was trapped there, causing pinholing. The cast of plaster was evidently so dense that the slip offered less resistance to the air when it was forced out by drawing water from the slip. When the less dense plaster cast was again used, the trouble immediately disappeared.

W. K. McAfee: A great deal of that is up to the mold maker. If he allows the plaster to set a little bit too far before he pours the mold in the cast, he is likely to get more of a tendency to produce pinholes in the finished ware.

GEO. CARTWRIGHT: I spent four or five years on that work myself. The trouble I have found is that they pour too many cases from one bucket of plaster. Eighteen or twenty cases out of one bucket of plaster cannot be poured and produce good ware. If 18 cases are poured, the first six cases will be hard and the next six molds may be fairly good, while the last ix molds will be soft.

We find that we get a great many pinholes in casting if we use the molds too long. As the molds wear we all know that they go to pieces, and when we find that they have a pinhole there will be a pinhole in the piece of ware nine times out of ten.

C. C. TREISCHEL: Has anyone had any experience with mechanical mixers for plaster?

E. H. FRITZ: We use the mechanical mixer in our work entirely. We have found it to be superior to the hand method of mixing plaster. It is a very simple proposition and is very much on the order of the mechanical mixer for cement. The spindle revolves at the rate of 250 r.p.m.

We have incorporated this method in our process specifications for making molds. Since the time we have adopted it we have found that our molds have considerably longer life and are very much more uniform.

C. B. YOUMANS: We have just started to do that in our mold shop and find it superior to hand work. We have a machine manufactured by the Hobart Manufacturing Company, Troy, Ohio. It is a regular dough mixer but we have adopted a special paddle to mix plaster.

K. M. SMITH: How do you test plaster to know when it is ready to pour?

C. B. YOUMANS: We have a regular kettle as ordinarily used and by placing your hand in it you can tell, just as in hand mixing.

E. H. FRITZ: I can answer that. Try various times of mixing and see what kind of a mix is obtained. You can very easily tell when you have mixed it too long from the way the plaster slip will pour. After the proper time has once been determined, standardize on that.

C. C. TREISCHEL: Has any one established standards whereby plaster and water are weighed?

E. H. FRITZ: We have done that.

C. C. TREISCHEL: Does that make any difference?

E. H. FRITZ: That is just as important as the mechanical mixing. The trouble which I described a few minutes ago was due to using too much plaster in the mix. It is all covered in our specifications.

W. K. MCAFEE: With regard to weighing the plaster, our molds are comparatively large and we only pour one mold or two halves of the same mold probably from the same kettle of slip. We use scales to get the proper amount of plaster to put in and the amount of water for a 2:1 ratio.

T. W. BLACK: The addition of marshmallow root helps to harden it and retards the setting and solution is made by boiling the root in water and adding to the mix when cool.

Question 24 What is the best practice with reference to mesh of lawns in preparing casting slips for various purposes?

C. C. TREISCHEL: Does that refer to pre-mixed or raw slips, or both? How about the size of lawn that is most satisfactory for raw slips, slips which are not made from filter press cakes or from pug mill blanks but are made from the raw materials. Can they be lawned through a 140-mesh? Do they have to go down to an 80?

W. K. MCAFEE: In order to start the discussion there are two general methods of making slip which will bear discussion. There is the raw method and the method with the filter press cakes.

We like to blunge the slip twice, principally because of this question of lawning. We make the slip up the first time about 20 ounces to the pint in order to get through a 120-mesh lawn. We pump part of that through a filter press and introduce it into the second blunger. We then mix the cakes from the filter press with this thin slip in order to bring the slip up to our finished weight of about $29^3/_4$ ounces. This finished slip will go through a 90-mesh lawn. If we mixed it all at once I do not believe we could get it through anything finer than a 90-mesh lawn. By the two methods we get it through 120, and we feel that we get a much cleaner body.

W. K. MCAFEE: The slip runs through the lawns too slowly to be practical.

C. C. TREISCHEL: Is not ball clay usually the thing in the body that makes it lawn harder? Has any one tried to wash the ball clay and use it in slip form in the mix?

K. M. SMITH: I have tried washing ball clay for a laboratory test and I found it quite difficult to put it through 100-mesh lawn. I ran it through the biggest series I could and tried to get as much out as I could before it reached 100.

C. C. TREISCHEL: This system is actually being used in plants. In that way they remove in a preliminary way a considerable amount of the material which causes the lawn to plug up. It is working very satisfactorily. I know of two cases where it is being used.

There is another thing in connection with that method that we want to consider and that is the fact that we can make the ball clay slip to a certain specific gravity and in that way insure a greater uniformity in the constituent which plays such an important part in the casting body. It is a means of control as well as one of cleanliness.

K. M. SMITH: Is it not true that the black ball clays will vary quite a lot in their lignite content? The point was that it would standardize the ball clay to a better extent.

W. K. McAfee: It eliminates the much harder question of water content.

K. M. Smith: What size mesh screen would you recommend for the final screen?

C. C. Treischel: It depends upon the subsequent treatment of the body. I know of one ground body that is made from the raw material that is screened through 180-mesh lawn. They are casting slip. I also know of a number that screen through an 80. It depends upon the preliminary treatment.

Question 25 What is the rôle of halloycite in casting? Does the use of it under certain conditions lead to troubles in mixing, casting and in firing? (This question comes from France.)

F. H. Riddle: I imagine most of us have at least seen halloycite. It has a hard surface and is white like kaolin, waxy and very hard. It will not slake down so readily in water and you practically have to grind it.

Naturally it has a high shrinkage and it is more colloidal. When it is worked it is very fine and spongy, and I imagine it would be useful in the same way that bentonite and some of those other materials are.

No one has mentioned this material as an aid in casting. It would be worth while possibly to try these things out. Halloycite can be obtained in the States because we have some of it in Detroit.

K. M. Smith: Prof. Cox, from whom I received my training, has done some very remarkable things with bentonite. I used about 5% of it with calcined china clay and ground it in a ball mill, enough to blunge it. I found that it would cast very well all alone and the resultant cast was quite hard.

I also took some grog made out of the dust from our sagger room, added some bentonite to it (about 5%), ground it in a small mill, and it came out like jelly. The large particles of grog would stay on top. They remained there until it hardened. It shows some wonderful possibilities not only in bodies but it is going to be very valuable as a floater in glazes that are high in frit, where we are having trouble with settling.

D. R. Kellogg: I heard somebody speak of that the other day and I believe they stated it was all tied up in patents. Do you know if that is true?

F. H. Riddle: There are a couple of patents which have been taken on it. One is used in spark plugs, I believe. McDowell has a patent on using a percentage of that. And then a concern of consulting engineers in New York has developed or control patents on its use in certain ways. I do not think the entire field is covered, however.

D. R. Kellog: It is used for many other things also. It is pretty well covered in soaps, etc., and as a suspending medium for flame-proof varnishes, etc.

F. H. RIDDLE: Part of ceramics is covered. The enameling people are using it in floating some of their enamels.

T. A. SHEGOG: I had something to do with Texas kaolin which is halloycite in nature. It would not slake in water at all even on prolonged boiling. If it is ground up with the mix, the mix cannot be lawned. The only way we could make up a body with it was in the ball mill. The body I made had 60% of English china clay replaced by this Texas kaolin. I added the non-plastic materials to the Texas kaolin, ground them separately and then ground the other plastics, the English china and ball clays. Then I mixed the two together, having lawned them separately first. The floating powers of Texas kaolin are extraordinary. After leaving that mix quite dilute for three days, intending to take off some of the water, I found that there was not any to take off. There was no sedimentation whatsoever, so that it has wonderful floating properties.

W. K. MCAFEE: Did you try to pump that or put it through filter presses? I understand it is very hard to work.

T. A. SHEGOG: You cannot put it through a filter press. It has been tried. A member of the committee who was carrying out these experiments tried that and failed utterly.

Then some one mentioned the casting. A body such as I have described can be cast but not commercially. It requires about three times as much water as an ordinary casting slip to get it into the liquid state and about two and one-half times as much dope. Furthermore, after it has been stirred up vigorously for an hour or two it thins up and can be cast, but it becomes entirely solid in the mold. To drain the mold it must be shaken vigorously, when it becomes fluid again and the surplus can be poured out. It takes about ten minutes to set up.

The pouring can must be shaken vigorously to pour another mold because it has become solid in the meanwhile. When all of these details are watched we get a wonderfully beautiful velvet finish on the ware. The feel of it is finer than anything I have ever seen. However, it is utterly uncommercial in large proportions.

E. SCHRAMM: I have made some experiments in connection with the same coöperative investigation. We were making vitrified ware. The body contained a replacement of 50% of English china by Texas kaolin. We did succeed in filter pressing it in an experimental plant, but I would not undertake to do it in a commercial way. I did not attempt to cast that body at all.

Following that up it appeared to me that the material might have some possibilities used in smaller quantity, so I made some pieces in which we got the Texas kaolin down to 5% of the body and made some casting slip with that. And even in that small proportion this material had a remarkable effect on the casting slip. I had to get the specific gravity down to an abnormally low value in order to bring the viscosity down to any practicable pouring point. Even so we did not get the viscosity down to that of our regular slip. The behavior was just as Mr. Shegog describes, very slow in setting, but giving a beautiful velvety cast and a piece which finished very nicely.

Question 26 What is the best method of plugging drain holes in the hollow cast ware?

W. K. McAfee: What I had in mind in that was in the case of hollow portions, that is thick portions of the ware, it is sometimes advisable to drain and leave hollow. Of course, there is a hole through which you drain it. For commercial reasons it is advisable some times to plug the hole.

I had in mind the hollow corner of our sanitary tank. We do not have a thick section there. We have a hollow at each corner of the tank plugged in the bottom. We find this more or less troublesome, sometimes causing cracks. Sometimes it will go through the biscuit kiln all right and crack in the glost kiln.

We have tried two methods of plugging. One is to use pugged clay of the same body taken from the filter press and pugged and used in a thoroughly moist state. We have also tried pouring in a little bit of slip against the plaster of the block in order to let it set up in the hole with the idea of getting a more homogeneous body. The casting method of plugging the hole did not seem to have any advantage at all over the sticking up method. Both gave us a little bit of trouble from time to time.

T. A. Shegog: We had that some time back in plugging handles of cast ware. I found that using the ordinary scrap but loading it first heavily with flint overcame that. It only occurred when the plug was pretty big. We worked it in by hand.

G. Cartwright: I think if there are any cracks, the air behind the plug causes that. Take a handle for instance. If we do not make the plug with a dull point we shall have air behind it and it will crack every time. If we make it into a point it will not crack around or across.

W. K. McAfee: What do you mean by "air behind it?"

G. Cartwright: If the hole is not completely filled with clay it will have some air in it.

W. K. McAfee: The hole goes through a body about half an inch thick. I do not believe you get our problem. You are talking about general ware and I am talking about sanitary ware.

T. A. Shegog: In the handles I referred to we only plugged one end. The handle is hollow right through, so there is no air cushion back of the plug to push it. I regarded it as due to the rate of contraction.

G. Cartwright: What did you use for the plug?

T. A. Shegog: We used the scrap clay. I am speaking of cast ware, of course. The plug was dipped in water so that it was really softer, has more contraction in it than the clay around the hole.

G. Cartwright: If it is too soft it will shrink more than the body around it

T. A. Shegog: Exactly; that is what happened, so I added the flint to get rid of some of the contraction.

W. G. Jackson: In dipping ware we have trouble sometimes in having dry spots on large pieces of hollow ware. The answer seems to be to reduce the amount of dope, but if we get it down too far it makes it hard to cast.

T. A. Shegog: Does it spot vertically?

W. G. Jackson: We simply have a point on large pieces such as jugs, numbers 6 and 12, where there is a dry streak on it.

G. Cartwright: You can pour them with a funnel and it will stop it. Take a funnel and run a long neck down within that as far as the bottom of the jug and pour the slip down the funnel. The man runs the slip down the side of the mold and it will be dry every time.

F. H. Rhead: We had the same trouble with some of our various porcelain products, and on investigating the matter we found that the slip would hit the side of the mold in one spot. We introduced the funnel and we had no more dry spots.

T. A. Shegog: That is the same case that was discussed a little while ago.

W. G. Jackson: We had no discoloration so I thought it was not the same thing.

T. A. Shegog: It is only in the big ware that there is discoloration. You get the dry spot every time.

Question 27 By using scrap over again in the casting body, what effect should a person expect to encounter? Would it require more dope the second time that you flocculate this clay? Would there be a change that would be noticed in the strength of the body? (About 15% scrap.)

W. L. Sample: We have found that we can introduce a large quantity of scrap (15 or 20%). We try not to let the scrap get dry before we put it in. There is not enough difference there to be noticeable.

H. Goodwin: With us it is very different. We find it better to dry the scrap and use in our raw charge (not scrap mill) about $2^1/_2$% of the 1500-pound charge. We experienced considerable trouble with our clay on the jigger when returning all casting scrap through the scrap mill, due in a great measure to this scrap probably getting pumped into the presses when little raw stock was in the agitators. We decided to eliminate casters' scrap for one week with good results, but if consistently mixed in raw mills its introduction into the body does not have any effect at all.

T. W. BLACK: We had a similar trouble. Dr. Mellor made a suggestion and I got rid of it entirely by using a little acetic acid in the blunger.

C. B. YOUMANS: That is why we use acetic acid. We weigh every bit of scrap that goes back into the blunging tubs and measure the acetic acid, so that we can dilute the scrap to the pH value of 6 every time.

W. K. MCAFEE: I take it that the discussion so far has centered around the comparatively dry scrap. Strictly speaking, the drain slip that is put back in the blunger is really scrap. It has to do with the change in amount of electrolyte present. If anybody would have asked me down in Atlantic City how much we could use I would have said 5%. I now say 25%. Our scrap piled up on us when we thought we could only use 5%. It is all gone now.

If you determine the amount of electrolyte used by the action or behavior of the finished slip, you automatically compensate for the varying amounts needed. This amount is, of course, a function of the electrolytes introduced in the scrap used.

Question 28 Why will two mixtures that have the same total shrinkage when formed by the dry process have entirely different shrinkages with the same amount of water added, when cast?

A. V. BLEININGER: In the dry process the total amount of water present is insufficient to permit of the free movement of the particles, and their dispersion from aggregates to individual particles is entirely out of the question. In the damp state required for dry pressing the clay particles remain as aggregates and are made to cohere superficially only by pressure. All kinds of granular material, of widely differing character can be compacted by pressure. The granular condition persists also during the firing process so that no decided variation between different clays should be expected, while the plastic condition develops the structural peculiarities of each material.

In casting we are dealing with the presence of a large amount of water which permits of the flotation of the particles. The aggregates therefore, having freedom of motion, may be dispersed by deflocculation. No two clays react alike as regards this dispersed state and no two of them produce the same structure which persists in drying and firing. They are bound to show differences in shrinkage. It is apparent, then, that while two clays may show the same total shrinkage when dry pressed, where they possess only a small water content and necessarily no freedom of motion, they are almost certain to differ decidedly when cast, and at liberty to develop all the possibilities of deflocculation and coagulation.

GETTING THE HIGHEST RETURN FROM KILN EQUIPMENT[1]

By John R. Green

ABSTRACT

Description of a recording pyrometer set up, the conditions to be observed and the benefits derived.

Introduction

The statement has been made that a large proportion of the labor saving and quality improving machinery and devices in the hands of operators today is not giving maximum return on the investment because of improper installation or insufficient attention in operation. The management is sold on the principle back of the installation but fails to pass on to the operating department the details in usage and upkeep. It is entirely possible that a part of this failure is the fault of the manufacturer to supply minute operating information and suggestions.

The purpose of this article is to review briefly the selection, installation and operation of the thermometer and pyrometer equipment with particular attention being paid to applying the instrument to everyday plant practice, and a consideration of the value of temperature-measuring equipment.

The first measurement of temperature effects in ceramic firing was the draw trial, next, the shrinkage bars, kiln settle, the Wedgwood gage, pyrometric cones and the Veritas firing rings. The pyrometric cones invented by Seger are the most important of the visual means of determining heat treatment in ceramic kilns. This system is popular because it measures more closely than anything yet devised the actual heat treatment of the clay. Pyrometers give information needed concerning the temperature conditions while the kiln is still black although under fire, and while the carbon is being burned out. We have come to the realization that some of the causes of losses in the finished clay products are due to mistreatment during these early stages of the firing, where actual temperature measurement and the rate of temperature increase are the only guides to good firing. For this work the indicating and recording pyrometer are the only satisfactory means of control.

The visual trial piece methods are continued in use because each gives information not possible to be obtained from others. The value of clay products, the cost of firing and the possible economies in firing are such that the management can well afford to use any or all of the systems known if by their use the firemen have more intelligent control. In the *Transactions of the American Ceramic Society* are lengthy discussions as to the respective merits of cones and pyrometer systems, all of which ended with the agreement that the work done by both were complements

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[1] Recd. Apr. 14, 1925.

of each other and that the use of all means available to control kiln firing were none too plentiful.

Consideration of pyrometers naturally come under three headings: (1) the equipment, (2) installation, (3) use.

The Equipment

Every pyrometer installation is composed of three units: (1) the thermocouple located at the point where temperature measurement is desired, (2) lead wires extending from the thermocouple to the instrument, (3) the indicating and recording instruments with suitable switching mechanism.

The thermocouples are (1) rare metal couples, giving long life and constant readings of temperatures to 3000°F, (2) base metal thermocouples at approximately one-fourth the original cost, of shorter life than rare metal when used at the same temperature but can be used in ceramic work for temporary temperatures as high as 1950° or 2000° depending upon atmospheric conditions in the kiln, *i. e.*, oxidizing or reducing.

A protecting tube is used to exclude gases from contact with the wires. Porcelain tubes of different compositions are used depending upon the temperature to be withstood. An outer protection of fire brick is a mechanical protection for the porcelain tube. The thickness of the crown or side wall will determine the length of thermocouple to be used. A 9-inch crown requires an 18-inch thermocouple and a 13-inch crown a 24-inch length.

All thermocouples for outside use should be made entirely weatherproof. Rain or snow in the porcelain tube or on the exposed terminals will make the readings inaccurate. A covering over the fire brick tube can at the same time hold the inner tube in exact position and not allow any moisture into the tube.

The wiring for all outside ceramic plant work will consist, in practically all cases, of No. 14 wire. This should be supplied with weatherproof insulation for open runs, and asbestos insulation wherever the wires pass over hot crowns, open crown holes or near fire boxes. There are two systems commonly used in wiring: (1) the individual return, in which two separate wires connect each thermocouple with the instrument, (2) the common return system in which one wire is made to answer for the negative return from all thermocouples, with individual wires from the positive side of each thermocouple to the instrument. The individual return is recommended unless the length of leads demands common return for economy.

The indicating and recording instruments must be simple in operation. Kiln firemen are not laboratory scientists, and an instrument must be placed in their hands that is simple and easy to operate or their support is lost. The instruments must be rugged in construction to withstand the severe conditions found in the average plant. All instruments should be encased in dustproof cases. The indicating instrument should have numbers that are easily read. A recorder of the continuous strip chart variety is the best because it is easy to read, and continuous in operation. It should be possible to mark directly on the chart at the time the record is being made, such notations as, water-out, carbon-out, settle readings, damper settings, or any other information which is directly related to the operation of the firing.

Installation

Thermocouples Where temperature is to be measured at one point only the thermocouples should be located in the crown as near to the center as possible. Three-quarters way up the crown usually is good practice.

The depth of insertion of the fire brick tube into the kiln depends on circumstance; 3 to 6 inches is common practice. In some cases the tubes are mounted flush or even recessed into the crown in order to use base metal for high temperatures. The farther the thermocouple extends into the kiln the more nearly will it record the temperature of the entire kiln.

The thermocouples in all kilns should be inserted to the same depth to obtain comparable readings. Quite frequently a kiln foreman will complain that one kiln requires an entirely different temperature schedule from another, and while this may be due to difference in design, draft conditions, etc., yet on inspection it is usually found that the thermocouples have been installed in widely different ways.

The heavy fire clay tube causes a time lag in the readings. Where greater sensitivity is required, as in some tunnel or chamber kilns, the ends of the fire clay tubes may be ground thin. This allows sensitive readings and yet does not expose the porcelain tube to the direct flames. The actual installation of the fire clay tube is a simple matter. A 3-inch hole is knocked out of the crown, the tube laid in with fire clay or clay mortar, and also supported by a curved flange that fastens onto the tube and rests on the crown.

In most heavy clay products work the actual measurement is the difference in temperature between the hot end of the thermocouple in the kiln, and the so-called cold junction at the head of the couple. The temperature at the indicating and recording instruments is assumed to be constantly near 70°F. The temperature where the thermocouples join the lead wires should be kept at 70°F. The weatherproof cover helps to maintain this constant temperature, although additional protection is desirable.

Where two thermocouples are used the second is installed through the base of the kiln, or into the flue leading to the stack.

The Instruments The instruments should be placed on a level with the eyes with good light and in a room used by the firemen as a resting place.

Use of Pyrometers

Any manager who expects to decrease his coal consumption and increase the quality of his ware simply because he has a pyrometer in the fireman's shanty is fooling himself badly. A pyrometer will never take the place of a good man on the business end of a No. 10 scoop. The fireman should not be a slave to the pyrometer.

In addition to temperature and time the fireman must consider draft in the stack and balance of pressure in the kilns both of which affect heat distribution. The fireman must consider the character of the kiln atmosphere, *i. e.*, oxidation or reduction. It is good policy to urge firemen to pay attention to kiln conditions rather than emphasize pyrometer readings. He will pay enough attention to the temperature because it is easy to do and he needs urging to watch the kiln itself in order that the correct proportion of attention may be given to each factor governing the firing.

Consider a pyrometer in the same class of equipment as the steam gage or speedometer. Analyzing the data from the boiler gage and the speedometer is simple because the results are immediately visible, while in the case of a kiln operation the results are not seen for several days. Some form of record must be maintained to check with the results observed when later the kiln is drawn.

Recording instruments give (1) a record of temperature development throughout the firing, (2) an incentive for the burner to make a perfect record.

At a glance it is possible to learn (1) the rate of temperature increase, (2) regularity in firing, (3) length of firing.

Evenness in firing is considered important. In the recent investigations by the Bureau of Mines fuel saving was obtained most often by regularity and frequency in firing. Quoting the report: "By firing little and often the temperature fluctuation is not so great and the temperature rise is more gradual. Whenever there is a drop in temperature it represents a time loss and fuel loss equal to the time and fuel necessary to regain lost temperature."

Water-smoking The water-smoking period of the kiln is one in which damage may be done and in which time and fuel may be saved. Speed and safety in the water-smoking period are dependent on draft and temperature.

During the water-smoking period the fireman should hold the top and obtain between 200 and 250°F in the bottom.[1]

A cold poker placed temporarily in the bottom of the kiln, and withdrawn to observe condensed moisture is probably the most common method of judging when the moisture has been driven from the kiln.

From this point on, the temperature of the kiln may be raised practically as rapidly as possible to the oxidizing period. The Bureau of Mines finds that "during the kiln investigation most of the time saving has been made during water-smoking. This has been done by improving the draft, by pushing the water-smoking along faster and by boosting the temperature to the oxidation period just as soon as the danger of water-smoking is over. Apparently it is the general practice among kiln firemen to hold back the temperature unnecessarily for a long time after the danger of water-smoking is over. When the bottom course of brick in a down-draft kiln has attained a temperature of 300° to 400°F (depending upon the nature of the clay) the temperature of the kiln can be boosted rapidly and safely to the oxidation period. If any damage has been done during water-smoking it has occurred under 300° to 400°F.

Oxidation Oxidation starts in the neighborhood of 900°F but progresses most rapidly between 1200° and 1400° depending upon the clay. Trial pieces drawn hourly will show the temperatures for each particular clay at which oxidation is most rapid, and also the length of time required for safe firing.

Soaking After the possibility of black core has disappeared, the firing may be pushed to the temperature of finishing or soaking. This temperature is usually far enough below the danger point of fusion to allow a good margin of safety. The kiln is held at this temperature until the desired amount of heat treatment has been given. This end point may be indicated in a variety of ways. With clays which have a wide vitrification range the completion of a predetermined firing schedule will be sufficient to assure a good firing. In firing clays which are more difficult to handle it is usual to test some property of the clay itself such as (1) color, (2) shrinkage, or (3) "ring."

In salt-glazing, pyrometers will indicate when the temperatures between saltings have recovered. This results in a saving in time, fuel and salt. Pyrometers make possible a similar positive control in flashing.

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[1] A recording thermometer may be used to take the bottom temperatures. A 2-inch iron pipe with a cap over the end is placed into the flue leading to the stack and just outside of the kiln extending into the flue for a distance of 12 to 18 inches. A recording thermometer of the gas-filled type is hung on the kiln bands above this pipe, the bulb being dropped into the end of the iron pipe. The thermometer should have a range of 0–600 or 800°F.

Cooling To obtain maximum kiln turnover they should be cooled as rapidly as the ware will allow. This is a matter of rate of temperature decrease. Opening crown holes and wickets should be scheduled by the temperature change rather than by time. A recording pyrometer will show the actual rate of cooling. Where fans are used to hasten the cooling the pyrometer must be watched even more carefully.

Results Possible with Pyrometers

Savings in Fuel

1. More efficient firing by maintaining even temperatures.
2. More effective firing by holding at the temperatures where the results desired will progress most rapidly.
3. Cutting total radiation losses by shortening the firing time.

Savings in Time and Increased Turnover

1. More effective and efficient firing shortens the firing time.
2. Rapid raising of temperature from the water-smoking period to the oxidation, etc.
3. Reduction of cooling time by the control of the cooling rate.
4. Records of idle periods will display opportunities for quicker turnover.

Decreased Depreciation of Kiln

1. Uniform rates of heating and cooling minimize expansion and contraction strains.
2. Indication of dangerous temperatures saves firebox and kiln linings.

Increased Quality of Ware

1. Eliminate "slabbed" ware by observing correct water-smoking temperatures.
2. Do away with "black core" and "swells" by using correct oxidizing temperatures.
3. Safeguard against overfired material by keeping away from the fusing temperature.
4. Eliminate checked or "dead" ware by the control of the cooling rate.
5. Produce uniform products from top to bottom, requiring less sorting.

Fuel, time, depreciation and quality may be figured in the common denominator—dollars and cents.

Brown Instrument Co.,
Philadelphia, Pa.

THE FAILURE OF THERMOCOUPLE PROTECTION TUBES IN GLASS MELTING FURNACES[1]

By Herbert Insley

ABSTRACT

The unusually rapid failure of thermocouple protection tubes when used in glass furnace atmospheres has been found to be due to reaction of the volatilized alkalis in the atmosphere with the aluminum silicates of the tube. Failure of the tubes is due either to differential thermal contraction between the outer reaction layer and the inner unaltered layer of the tube on cooling or to actual corrosion and dripping away of the tube. It is suggested that the use of a much higher percentage of alumina and lower percentage of silica in the tubes may prevent failures from this cause.

It is well known that porcelain thermocouple protection tubes deteriorate rapidly in a glass furnace atmosphere if they are not shielded by additional refractory coverings. The usual method of protection is to fit the tube into a hollowed-out silica brick which projects into the tank and although there are obvious disadvantages in such an installation, they are more than counterbalanced by the longer life of the protected tube.

Previous investigations[2] have shown that corrosion of glass tank refractories may be caused by the action of the furnace atmosphere and it was thought that the failure of the thermocouple tubes might be due to the same cause. Microscopic examinations of thermocouple protection tubes were made in order to see what structures, comparable to those developed in refractories under the same conditions, were present. Samples of unused tubes and tubes used in other types of ceramic kilns were also examined. Many of the tubes examined were made at the Bureau of Standards of a batch developed there, the composition as calculated from the batch weights being: SiO_2 34%, Al_2O_3 64%, K_2O 2%. The glaze applied to the tubes had approximately the following composition after calcination: SiO_2 75%, Al_2O_3 15%, CaO 5%, MgO 1%, K_2O 4%. The tubes were fired to cone 18, a temperature of 1480°C having been reached after approximately 48 hours' firing.

There were available for microscopic examination: (1) unused tubes, (2) tubes which had been used at 1450°C for 72 hours in a kiln for testing refractories, and (3) tubes used for about a week in a pot furnace whose temperature was, in general, 1425°C and in which optical glass was being melted.

(1) The unused tubes were found to be composed of mullite ($3Al_2O_3.2SiO_2$) crystals, glass, and dehydrated, partly transformed clay matter. There was only a small amount of glass present, which may account for the fact that the mullite crystals were short, stubby prisms and not the long, slender needles usually found in porcelain bodies. The glaze had

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[1] Published by permission of the Director, Bureau of Standards.

[2] Insley, *Jour. Amer. Ceram. Soc.*, **7**, 583–93 (1924).

penetrated the body to a slight extent, as indicated microscopically by an increased percentage of glass near the surface. Mullite crystals at the junction of body and glaze were small and scattered.

(2) The cross section of the hot end of the tube exposed to 1450° C for 72 hours showed three very distinct zones: (*a*) an outer zone of glass about 0.25 mm. thick which undoubtedly represented the glaze; (*b*) a middle, porcelain-like zone which was quite vitreous and extended about half-way through the tube; and (*c*) an inner, less vitreous zone. The microscopic examination showed the outer zone *a* to be composed entirely of glass with an index of refraction of about 1.515. At the junction of the glaze and zone *b*, long, well-formed needles of mullite projected into the glaze. The middle, vitreous zone *b* was composed of stubby prisms of mullite and a fair quantity (perhaps 50%) of interstitial glass. No other constituents were observed. The inner, less vitreous zone *c* contained stubby prisms of mullite, much smaller than those in the middle zone, and a much smaller percentage of interstitial glass than the middle zone. The vitrification in the middle zone was evidently due to the absorption of part of the glaze by the body.

(3) The tubes from the glass furnace were not used longer than one melting period of seven or eight days and the furnace was maintained at a temperature of about 1425° C during most of the time. All the tubes showed the same characteristics and all failed in the same way. It is noteworthy that they apparently remained intact until the final cooling took place when a part of the hot end broke off. At or near the hot end of the tube the cross section showed two distinct zones; an outer very vitreous zone and an inner less vitreous zone. In some cases the hot end was entirely composed of the more vitreous material. Toward the cooler end of the tube the more vitreous outer zone gradually decreased in thickness until it disappeared. A microscopic examination of a thin section showed very striking differences in the structure and composition of the two zones. (Fig. 1.) The inner less vitreous zone was composed of mullite and glass with perhaps a slightly larger percentage of glass and a somewhat better development of the mullite crystals than the unused tube. The outer vitreous zone contained small but well-formed plates of corundum (Al_2O_3) embedded in glass whose index of refraction was about 1.525. The amount of corundum was apparently about the same as that of glass. In many of the pieces of tube the outer and inner zones could be easily broken apart because of the formation of a crack at the junction.

A commercial protection tube which had been used in the Bureau glass melting furnace for one melting period (about a week) was also examined. In this tube three zones were observed which represent the portions exposed to different conditions: *a*, a non-vitreous portion at the cold end of the tube still covered with the original glaze, representing the unaltered tube;

b, a slightly more vitreous zone nearer the hot end of the tube, and *c*, a vitreous outer zone surrounding zone *b*. About one inch of the extreme end of the tube within the furnace was broken off, the broken edge showing only zones *b* and *c;* zone *a* made up the cold end and became thinner toward the hot end until it disappeared. It was composed of small, rounded, more or less prismatic crystals embedded in glass, the crystals resembling mullite in their optical properties. Long needles of mullite extended from the body into the glaze. Zone *b* was composed of glass with an index of refraction between 1.52 and 1.53 and small, well-formed plates of corundum less than 0.05 mm. in greatest dimension. Zone *c* was composed of glass and an artificial soda-lime feldspar with the optical properties of labradorite. Quantitative measurements indicated that this feldspar was composed of about 30% of the soda feldspar ($NaAlSi_3O_8$) and 70% of the lime feldspar ($CaAl_2Si_2O_8$).

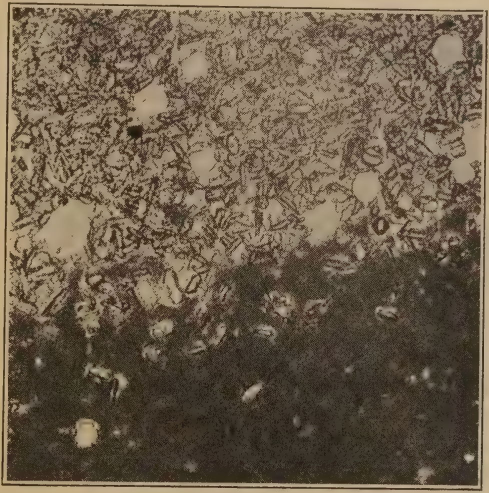

Fig. 1.—Photomicrograph of Bureau of Standards thermocouple tube used in a pot furnace melting optical glass. The contact between the lighter vitreous zone composed of corundum and glass and the darker, less vitreous zone composed of mullite and glass, is shown; magnification, 100 ×.

Experimental tubes containing silica and alumina in such proportions that after firing they would have a composition like that of sillimanite ($Al_2O_3.SiO_2$) were made by a porcelain manufacturer. One of these tubes was used in a Bureau of Standards pot furnace and another in a commercial pot furnace. The former lasted for seven or eight days, but was found to be cracked when the furnace had cooled down. The end of the tube which had not been exposed to the heat was composed of well developed mullite crystals, much larger even than those found in well fired clay bodies. The crystals were embedded in a relatively small amount of glass. The end of the tube exposed to the heat was covered with a brown vitreous skin of glass full of hexagonal plates of corundum. This layer covered an inner zone which was essentially like the cold end of the tube in its constituents but which was more vitreous in appearance and contained more glass and less mullite. The end of the tube within the furnace was much more brittle than the end outside of the furnace.

The tube of the same type which had been placed in a commercial pot furnace had probably been exposed to more severe heat treatment and more corrosive action. The end was entirely gone, having fluxed or broken away. A microscopic examination of the tube at the break showed that this portion was entirely composed of corundum and glass. The corundum was arranged in overlapping parallel plates which were approximately perpendicular to the outer surface of the tube.

Causes of Failure

A comparison of the results of the microscopic examination made on tubes exposed to glass furnace atmospheres and on tubes exposed to kiln atmospheres at temperatures approximately equivalent shows that many of the constituents are different in the two cases. The tube used in the kiln for testing refractories still retained its original glaze and contained no corundum. The tube used in the glass melting furnace was covered with a crust of corundum, it contained a relatively large amount of glass, and it was thoroughly vitrified in the portion exposed to the heat and atmosphere of the furnace.

Since all of the thermocouple protection tubes used in glass melting furnaces had been exposed to the atmosphere of the furnace only and had not been in contact with the molten glass itself, they were subjected to practically the same conditions as refractories above the glass line in melting furnaces. A comparison of clay refractories and the thermocouple tubes exposed to glass furnace atmospheres shows a great similarity in structure and in the reaction products. In both materials the action of the soda or sodium compounds in the gases and dusts on the aluminum silicates causes the formation of a glass (a liquid at furnace temperatures) which Wilson[1] on the basis of chemical analysis, decided had a composition of approximately $Na_2O.Al_2O_3.5SiO_2$. Any alumina in excess of this composition forms crystals of corundum which are present as crusts on the surface of the material. The one tube mentioned above, in which there was an outer layer of soda-lime feldspar superimposed on the layer of corundum and glass, was probably exposed to batch dusts containing so much lime that the feldspar formed had a melting point above the temperature of the furnace and was easily crystallizable.[2]

In commercial pot or tank furnaces where a high temperature is maintained continuously and where the furnace atmosphere is constantly full of batch dusts and volatilized materials, the thermocouple tubes are actually corroded by the reaction between the aluminum silicates of the tube and the substances in the atmosphere. If the percentage of silica is high, a large quantity of liquid is formed on the tube. This liquid drips away, carrying corundum crystals with it until the tube is eaten through.

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[1] *Jour. Soc. Glass Tech.*, **2**, 197–213 (1918).

[2] The melting point of a feldspar of this composition (soda feldspar 30%, lime feldspar 70%) when pure is about 1495° C. Bowen, *Amer. Jour. Sci.*, **35** [4], 583 (1913).

In experimental furnaces like those used at the Bureau of Standards, the melting period is comparatively short. Only the outer portion of the tube is affected and the liquid formed usually does not drip away. After use, such tubes have an outer glassy layer in that part exposed to the high temperatures and the furnace atmosphere. There is often a cleavage plane between the outer and inner layer so that the outer layer falls off or may be picked off easily with the fingers. Cracks extend through the tube and often the entire end of the tube breaks off. The fact that tubes in use in experimental furnaces fail during the cooling period suggests at once that the splitting away of the outer layer of the tube may be due to differences in thermal expansion between it and the inner layer. G. E. Merritt, of the Bureau of Standards, made thermal expansion measurements on pieces of the outer and the inner zones of the used thermocouple tubes the results of which are shown in Fig. 2. From these curves it is seen that during the cooling of the furnace, the outer zone tends to shrink more than the inner zone. There is a weakening at the junction and the outer zone cracks lengthwise in order to relieve the tensile stresses.

Suggested Improvements in Thermocouple Protection Tubes

The microscopic evidence shows clearly that the action of the dusts and gases in the furnace atmosphere on the thermocouple tubes causes the formation of a glass and corundum (Al_2O_3). The formation of the glass, which is a mobile liquid at these furnace temperatures, is apparently the cause of the failure of the tubes.

A possible method for preventing the formation of a large amount of silicate liquid suggests itself; that is, by increasing the ratio of alumina to silica in the body so that only enough silicate liquid is formed after the reaction with the soda in the furnace atmosphere to form a matrix in which the excess alumina may crystallize.

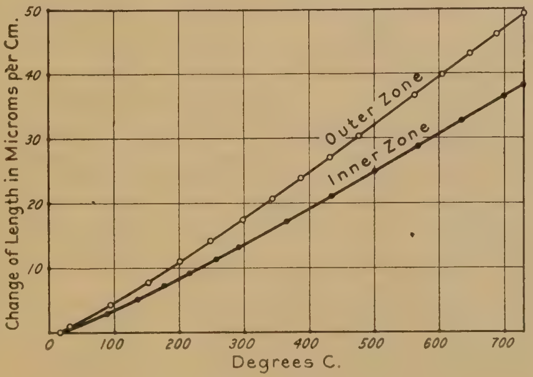

FIG. 2.

With this in view, a batch was made up of calcined alumina, ball clay and feldspar in such proportions that the body would have a composition of approximately 14% SiO_2, 85% Al_2O_3 and 1% of alkali. The body cast satisfactorily, but was somewhat weak in the dried state and showed excessive shrinkage when fired. A tube of this composition was placed beside a tube of the usual type in the pot furnace at the Bureau. At the end of the melting period the experimental tube was somewhat deformed but still intact, while the other had cracked badly and pieces of the outer layer had spalled off. There were no traces of spalling and no cracks in the high alumina tube, but the surface was crusted over with minute corundum plates. Through the kindness of A. R. Payne, of the Hazel-Atlas Glass Co., another tube of the same type was placed in a tank melting bottle-glass. The tube was mounted without protection in the end of the tank about midway between the two filling-in dog houses, 18 inches above the glass line, and projecting 6 inches into the tank. It lasted about five days after the temperature had reached about 1430°C and two days after the filling with batch had begun. According to Mr. Payne's statement, this is about the average length of life of the ordinary unprotected pyrometer tube. It was thought, from the appearance of the tube used in the Bureau furnace, that failure might have been caused in part by mechanical weakness. It is now planned to make up a batch eliminating the feldspar and substituting "fused" alumina for calcined alumina.

Summary

Thermocouple protection tubes used in glass furnaces fail much more rapidly than the same tubes used in the ordinary ceramic kilns even though temperatures may be practically the same. Microscopic examination and other evidence shows that the volatilized alkalis and the alkaline dusts in the glass furnace atmosphere react with the aluminum silicates of the thermocouple tube, causing the formation of a liquid with a composition approaching the formula $Na_2O.Al_2O_3.5SiO_2$. In this liquid excess alumina crystallizes as corundum. Failure may take place in two ways: (1) If the reaction between the alkalis in the furnace atmosphere and the aluminum silicates of the tube takes place intermittently for short periods of time, the reaction liquid may occupy only the outer layer on the hot end of the tube. The solidified liquid has a different thermal expansion than the interior of the tube and cracking and breaking take place during cooling. (2) If the reaction takes place uninterruptedly at high temperatures, the liquid formed drips away and the tube is actually corroded.

The use of much higher percentages of alumina in the tubes than have heretofore been used is suggested in order that after reaction with the alkalis there may be a large amount of crystalline corundum on the surface of the tube and a small amount of liquid silicate.

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ORIGINAL PAPERS

SOME FEATURES OF TANK BLOCK COMPARISONS[1]

By F. S. Thompson and H. I. Vormelker

ABSTRACT

The life of glass blocks can be increased by lower furnace temperature obtained by increasing the area of melting chamber, and by insulation of the walls. Analysis and physical tests of clays and of blocks made from them are compared with results of service test but data does not warrant conclusion.

Introduction

The glass house men present at the various meetings of the American Ceramic Society during the past year seem to be of the unanimous opinion that better tank blocks for glass furnaces is the most outstanding need of the industry. Some have gone so far as to point out that at the present rate of negative acceleration the life of our tanks will soon be zero.

The question of better refractories is an extremely important one, and the search should be pushed without stint; but we should not overlook the fact that a great many of the vituperations that are heaped upon the heads of the manufacturers of tank materials are not merited. All of these companies are as anxious to produce long service products as we are to receive them and we all know that several of the companies maintain expensive research departments for the purpose of developing the best product from the materials available.

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb., 1925. (Glass Division.)

Factors Determining Service Life of Blocks

It has often been pointed out that the services of any particular tank should be given in tonnage produced per fire and not in total months of fire. It is the fair thing to do; yet, we have great difficulty in overcoming our tendency to compare one fire with another in a given tank by the number of months' duration of each. We have often heard tank men complaining that they are now receiving only eight months' service from a furnace that formerly gave twelve. As a usual thing no mention is made of the increased tonnage.

The life of a tank block is determined by various factors over some of which the tank block manufacturer has no control, such as, the temperature at which the tank is operated, the ratio of tank block surface to the tonnage produced, the design of the tank, and the composition of the glass. The factors which he does control are: the materials, the manner in which they are incorporated and the firing of the blocks. We shall take up each in turn.

Furnace Temperature

It is a well known fact that a clay substance softens and deforms at a much lower temperature than that required to fuse it completely. This softening point varies in different clays with variation in physical state and kind of minerals present. The temperature of beginning and the temperature range of this softening point have a definite bearing on the wearing ability of a tank block. For example, if a given tank block begins to soften at 1385°C and a furnace is operated above that point the corrosion will be much more rapid than it would be were the tank operated at a temperature of 1380°C. Furthermore, disregarding the softening point of clay, we all know that the speed of a chemical reaction is greatly accelerated by increase of temperature. At 100°C clay and glass in contact would remain clay and glass indefinitely, but at 1800°C there would be, in a few moments, an intersolution. After 1200°C the acceleration of solution is increased with increase in temperature. Since glass is melted in this rapidly accelerating period, it is a self-evident fact that the furnace should be operated at the lowest temperature consistent with production of the maximum quantity of good product.

Non-uniformity of Temperature in Tank

It is quite possible that the melting end of a tank could be operated at a temperature but little higher than the refining end if the entire capacity of the space were put to actual use. We know that the bottom portions of the glass move very slowly if at all. We know that glass actually passes through a tank from doghouse to production in one-third the theoretical time. The bottom portion is sluggish because it is viscous and it is viscous because it is cold.

One remedy for this condition has been suggested by Mr. Brownlee of the Buckeye Clay Pot Company. His proposal for insulating the bath of glass tanks has been the basis for several discussions pro and con. Most of the criticisms that we have heard and read are in opposition. Most of them have not mentioned the most important feature that might be expected to result from tank insulation, that is, a lower operating temperature in the melting chamber. We base our assumption of a lower temperature on the increase of useful space made available.

Figure 1 shows a cross-section of a portion of insulated side wall and bottom. In the side wall the dotted line indicates the inside face of the block after several months of firing. This drawing is based on photographs of blocks removed from a tank melting soda-lime glass. If the difference in the degree of corrosion between the top and bottom is due to the difference in temperature it might be possible that with insulation, as shown, the wall would wear down more evenly. The wearing away at the flux line would be retarded by a lower operating temperature and the rate of solution on the lower part of the face would be increased by a higher temperature and more activity in the glass.

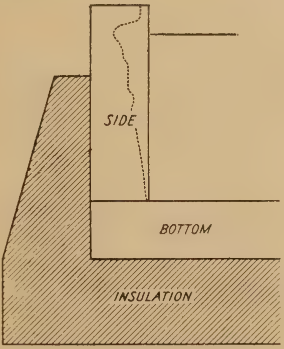

FIG. 1.

Another point that has been overlooked in the criticisms of this theory is the fact that no insulation is placed at or near the metal line. In fact this area should continue to be cooled by artificial means. With this arrangement we would have the region of greatest attack, operating as it does today with the exception of the advantage of a lower temperature. The lower portions of the side wall and the bottom would, of course, wear away more rapidly but there would be the advantage of the use of a greater volume of the tank capacity.

Ratio of Capacity to Production The control of the temperature required in a continuous tank for melting good glass lies largely in the design of the furnace. It is, of course, possible to design a furnace to be used below its rated capacity, but this is not usual nor is it desirable. The increased fuel cost would not justify operating a tank below capacity. It is, however, desirable and economical to use a furnace at its rated capacity but not to overload it. Overloading requires use of increased temperatures with consequent shorter life of the tank. The argument is often advanced that it is economical to overload a tank and overcome the handicap of short life with increased production and lower fuel cost. This may be true in some cases but not a few experiences have proven that this often is an error.

A certain furnace was producing 22.9 tons each twenty-four hours on an average of eight months. This tonnage was produced from a melting area of 296 square feet which is equivalent to 12.9 square feet to each ton. The furnace melting chamber was carried at 1410°C or higher for the entire run. This temperature was necessary to produce this tonnage of good glass. The coal consumption amounted to 22 tons per day.

At the end of the fire the melting chamber was enlarged to an area of 358.5 sq. ft., an increase of 62.5 sq. ft. With this change the average daily production has been exactly the same as formerly, 22.9 tons per day. But the temperature at the melting end is now 1350° to 1360°C (50° lower) and the average daily consumption of coal 19 tons or 3 tons less per day. These comparative figures, based on actual production and operation records, prove that there are times when a large furnace can be operated with less fuel than a smaller one.

TABLE I

	Melting area	Tons per day	Sq. ft. melted area per T. melted	Av. coal per day	Temp., degrees C
1st fire	296	22.9	12.9	22T	1410–1440
2nd fire	358.5	22.9	15.6	19T	1360–1380

It is quite apparent that the furnace blocks will give a far better account of themselves at the lower temperature than at the higher.

Glass Composition It is commonly held that the different glasses have different corrosive effects on tank blocks; that is, a given tank might last for fifteen months on one variety of glass and eight months on another. Yet most glass men buy and receive, and most clay works sell and ship, the same block for all glasses. It is our belief that for each glass there is a refractory most suitable and that an effort should be made to determine the character of a refractory most suitable to each type of glass.

Investigation of Clays and Blocks

In January of 1924 we received sample blocks and a small quantity of the prepared clay with which the blocks were built. We subjected the clay to various physical and chemical tests. The results indicate the wide degree of variation in the raw materials used for tank block construction. Not only were the physical characteristics widely variable but the chemical analyses also showed the products to be indeed markedly distinctive.

Chemical Composition The following table gives the silica, alumina and iron oxide content of eight standard blocks that are on the market today, and the approximate analysis of the clays, unfired, of which each block was made.

TABLE II

	Tank block			Unfired clay		
	SiO_2	Al_2O_3	Fe_2O_3	SiO_2	Al_2O_3	Chem. water
1	77.8	21.0	0.7	72.7	20.0	6.7
2	77.4	17.8	2.3	73.4	17.1	5.0
3	76.3	22.0	1.3	71.9	21.0	5.3
4	68.7	27.6	2.6	62.8	25.3	8.6
5	67.3	29.6	2.1	61.1	26.9	8.9
6	63.8	28.2	3.9	....	....	...
7	73.4	22.8	1.8	....	....	...
8	56.5	39.0	2.1	50.1	34.6	11.2

Physical Tests of Clays

Drying shrinkage of the raw clays also showed a range of differences. To obtain these figures ten bars of 1-inch square cross-section and 6 inches long were made up of equal parts of standard sand and sample clay. Marks were laid off near the ends of the bars with a razor blade and the intervening distance measured. The sample bars were then dried at room temperature and at 120°C and measured again. The following figures show the average shrinkage of each of the clays from which the eight blocks in question are made.

TABLE III

Clay	Per cent linear shrinkage	Rupture modulus, lbs. per sq. in.	Clay	Per cent linear shrinkage	Rupture modulus, lbs. per sq. in.
1	1.81	104	5	2.57	140
2	3.48	427	6	2.85	178
3	3.70	258	7	2.45	135
4	2.96	156	8	2.61	187

The modulus of rupture of these same clays was obtained according to the procedure of the American Ceramic Society Standard Test. The bars were 7 inches long and approximately 1 inch square in cross-section. They were composed of equal parts of standard and sample clay.

From this wide field of selection the block manufacturer has been choosing his raw materials. Usually his choice rests upon expediency and custom; that is, he chooses a clay that always has given a certain amount of satisfaction and is easy to prepare, mold, dry and fire. Since a great many clays of divers compositions fill all these requirements, it follows that our tank blocks are not likely to be of uniform composition.

The question of the effect of the composition of the tank block upon its quality of service naturally arises. It is reasonable to assume that compounds or solid mixtures of different composition will react differently in contact with a definite reagent; that is, we might readily expect that a block containing 77% silica will show a different resistance to corrosion by glass than one containing 50% silica. We might also look for different performances from two blocks containing, respectively, 7 parts of Fe_2O_3 per thousand and 40 parts of Fe_2O_3 per thousand.

Therefore, we might be justified in assuming that these different blocks of varying composition would show different degrees of corrosion in contact with the same glass. If the degree of corrosion is different one must be the greatest and one the least or, in other words, one must be the poorest and one the best in contact with that particular glass.

It would seem, therefore, that a good starting point in the search for better blocks would be the selection, by each manufacturer, of the type of block best suited for his glass from among those already on the market.

We are well aware that it is an unwritten law of the glass house that the only real test of a tank block is to build it into the furnace and find out how long it will last.

This may be the only trustworthy test, but we should not be deterred from seeking other methods of determining the wearing qualities of a block in a few hours or days instead of a few months or years. We are now seeking such a method. We realize that our efforts result in but a very small fraction of the information necessary for a definite conclusion. Satisfactory results will be attained only from a cumulation of data.

Assuming that the greater part of the destruction of the tank block is due to physical abrasion and chemical action between the clay and the glass we set about to obtain some method of comparing tank block solubilities in glass. There are other properties that affect the life service of a block but these two factors seem to be the most important. Inasmuch as porosity has a relation to each of these two properties the figures showing the percentage pore space were determined.

The investigations by R. M. Howe, S. M. Phelps and R. F. Ferguson dealt with the action of slag on various refractory materials. This can be considered a subject closely akin to the one we are discussing.

Solubility Test A quantity of chips from the tank block were pulverized in a ball mill and screened. That which passed through the 180-mesh and stayed on the 200-mesh sieve was mixed with a soda-lime glass batch in the proportion of three to one (75% clay—25% batch). This mixture was pressed dry into plaster molds to form cones the size and shape of Orton Standard cones. The mold and contents were placed in an electric muffle furnace and heated to 650° to frit them into solid form of sufficient strength to permit handling.

Two of these cones were then placed on a pat with a series of Standard Orton cones. The pat was placed in a surface combustion furnace and the temperature raised at the rate of 10° per minute. When the test cones were bent to the pat the gas was turned off and the result noted in terms of Orton cones.

This test is based on the assumption that the cone composed of the mixture the most readily intersoluble would fail first. The results are shown in Table IV.

TABLE IV

	Solubility				
	Failed at cone	Approx. temp., °C	Abrasion per cent loss	Per cent porosity	Apparent density
1	7—	1265	6.2	23.0	2.25
2	6	1250	9.9	23.6	2.24
3	10—	1325	8.4	23.9	2.26
4	12—	1325	60.1	28.1	2.18
5	6	1255	4.6	23.7	2.23
6	8	1290	16.3	26.5	2.19
7	8	1295	11.6	30.1	2.15
8	14—	1400	40.1	23.0	2.28

Abrasion Test A portion of the sample block was broken up into pieces as near cubical as possible, approximately $1^1/_2$ inches. Selected pieces were then placed in a ball mill and given a preliminary grinding. This operation ground off the sharp corners and reduced the pieces to a more or less rounded shape. From among these pieces were chosen those of most uniform size and shape.

One hundred and fifty grams of the chosen pieces were placed with 1000 grams of flint pebbles in an 8-inch ball mill and rotated for a period of two hours at a rate of 80 revolutions per minute. The charge was then removed and placed on a 10-mesh screen and subjected to the action of a Tyler Ro-Tap until nothing remained on the screen but the flint pebbles and the remaining portion of the sample pieces. The latter were removed and weighed and the loss noted. The percentage of this loss gave some idea of the resistibility of the block to abrasive action.

The results of this test on the eight blocks are shown in Table IV.

Two samples of English tank block showed porosities of 17.2% and 17.8%, respectively, although they were of porous appearance. On the other hand we examined a clay block and a sillimanite piece that were made and sold as "dense" material. They showed porosities of 30.25% and 39.4%, respectively. Other instances that have come within our observation have indicated that efforts to make a dense block have generally resulted in a higher porosity and, of course, less density. However, if the pores be sufficiently minute the block might be considered as equivalent to one of low porosity even though it measured 40%. The surface tension of the glass would probably be sufficient to prevent penetration.

Such figures as the foregoing obviously are not a complete basis for final conclusions. We have desired merely to point out the marked differences in the principal characteristics of commercial blocks. Each one of the tests described shows that the commercial blocks now on the market vary in properties between wide limits.

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ENAMELING DEFECTS DUE TO CAST IRON

By A. I. Krynitsky[1]

ABSTRACT

A discussion of Malinovszky's paper on enameling defects due to cast iron. Problems are suggested for further investigation on the subject.

A. Malinovszky has published a very interesting paper "Enameling Defects Due to Cast Iron."[2]

In the beginning of his paper Malinovszky states that "blisters, if caused by the iron, seem to be governed by the condition and size of the graphitic carbon. The presence of slag or dirt in the castings or at the surface of the casting also can cause chipping, lifting, black specks and blisters" and in the summary he adds that "it seems that as soon as the combined carbon is high and if temper carbon is present the blistering of the enamel is certain."

These important conclusions which are the essence of the paper appear to the writer as not having been sufficiently substantiated. For example, in describing Fig. 7 the author writes: "This sample was taken from a perfect enameled tub. The sample has abundant graphitic crystals, most of which are arranged with flat face parallel to the enameled side. Free cementite occurs sparingly and is more abundant toward the enameled side."

It is to be regretted that chemical analysis and magnification are not reported for each micrograph. From the table of chemical analysis given for three tubs before and after enameling it follows, however, that there is a substantial loss in combined carbon after enameling and that in almost all cases, except that of the $5^1/_2$-ft. flat rim tub before enameling, we have to deal with the hypoeutectoid irons and therefore ought to expect the presence of free ferrite rather than free cementite. It is assumed that the magnification in the micrographs was about 100 ×.

On examining Fig. 7 and bearing in mind the foregoing remarks one would interpret the micrograph as representing a mass of pearlite, a small amount of ferrite and comparatively large flakes of graphite.

There is another sample of iron reported by Malinovszky as giving no trouble from blistering and being probably a very good iron for enameling; it is represented by Fig. 3. Examining the structure in this figure we notice again the presence of a large amount of pearlite, comparatively small amount of free ferrite (or free cementite?) and small graphite flakes.

It is not believed that these two examples could lead us to such a conclusion as that which the author offers in his summary; *i. e.* "It is clearly shown that a low combined carbon and an evenly distributed graphitic carbon in very minute state will show no signs of blistering."

Referring now to his Fig. 6 we may note that, although it is very probable

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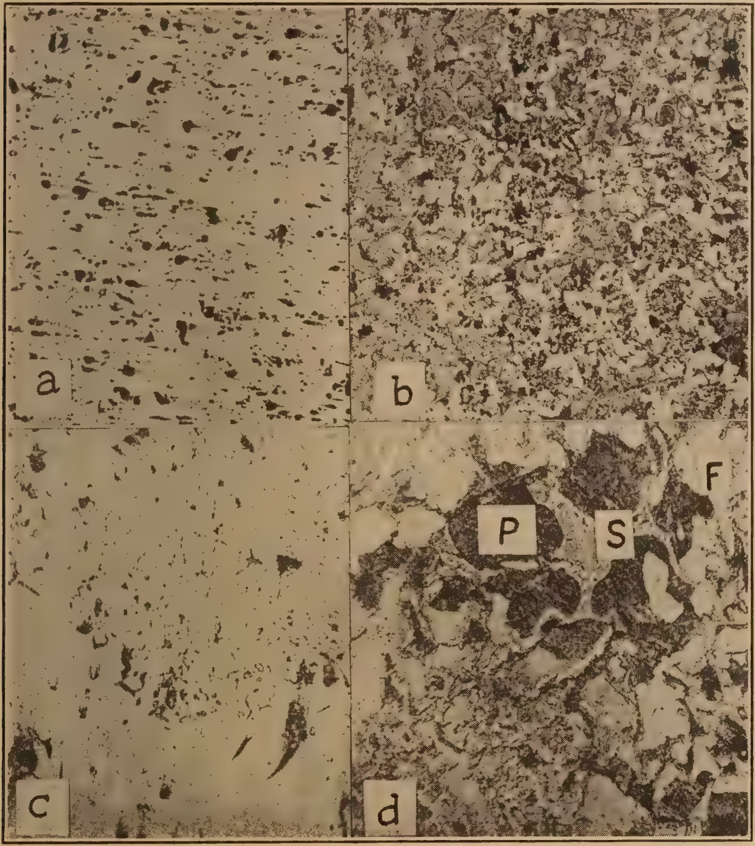
[1] Recd. July, 1925.

[2] *Jour. Amer. Ceram. Soc.*, **8** [1], 72–8 (1925).

that temper carbon may cause blistering, this figure appears not clear enough as to warrant such conclusion.



a—Polished. × 100 *c*—Polished. × 500.
b—Etched in 5% picric acid. × 100. *d*—Etched in 5% picric acid. × 500.
F—White, structureless constituent—ferrite.
P—Dark constituent—pearlite.
S—White, mottled (dotted) areas—binary phosphide eutectic, so-called "Steadite." It contains according to Stead about 10% P and 90% Fe.

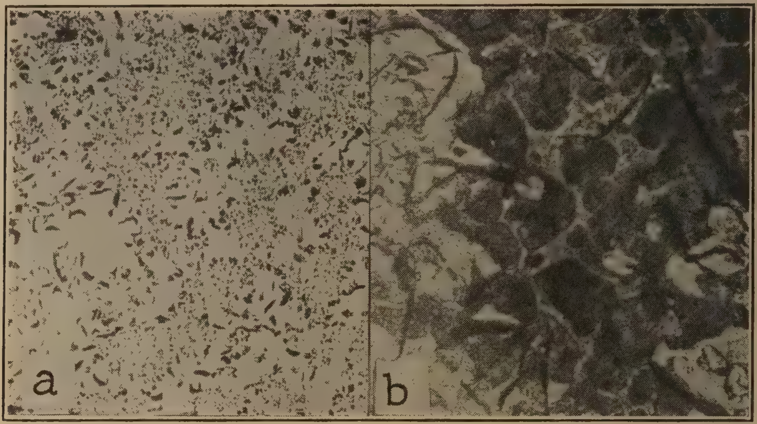
FIG. 1.—Heat No. 1.

Effect of Iron Composition and Crystallization

While it should be understood in the discussion below that there are not enough data, as yet, on hand to warrant any definite conclusion, still it was thought that the following observations will be of interest in connection with the foregoing discussion.

A number of samples in the form of plates 3″ x 6″ x $^3/_{16}$″ cast in green sand molds and prepared for enameling test were ground down about 0.01″

on the drag side and examined microscopically. Micrographs given below show the structure of the drag side of specimens before enameling. They represent 3 different heats of the same iron and they agree fairly well with the microscopic observations made on the cross-sections of the similar specimens.



a—Polished. × 100. *b*—Etched in 5% picric acid. × 500.
FIG. 2.—Heat No. 2.

The chemical analysis and proximate structural composition are given in the table below:

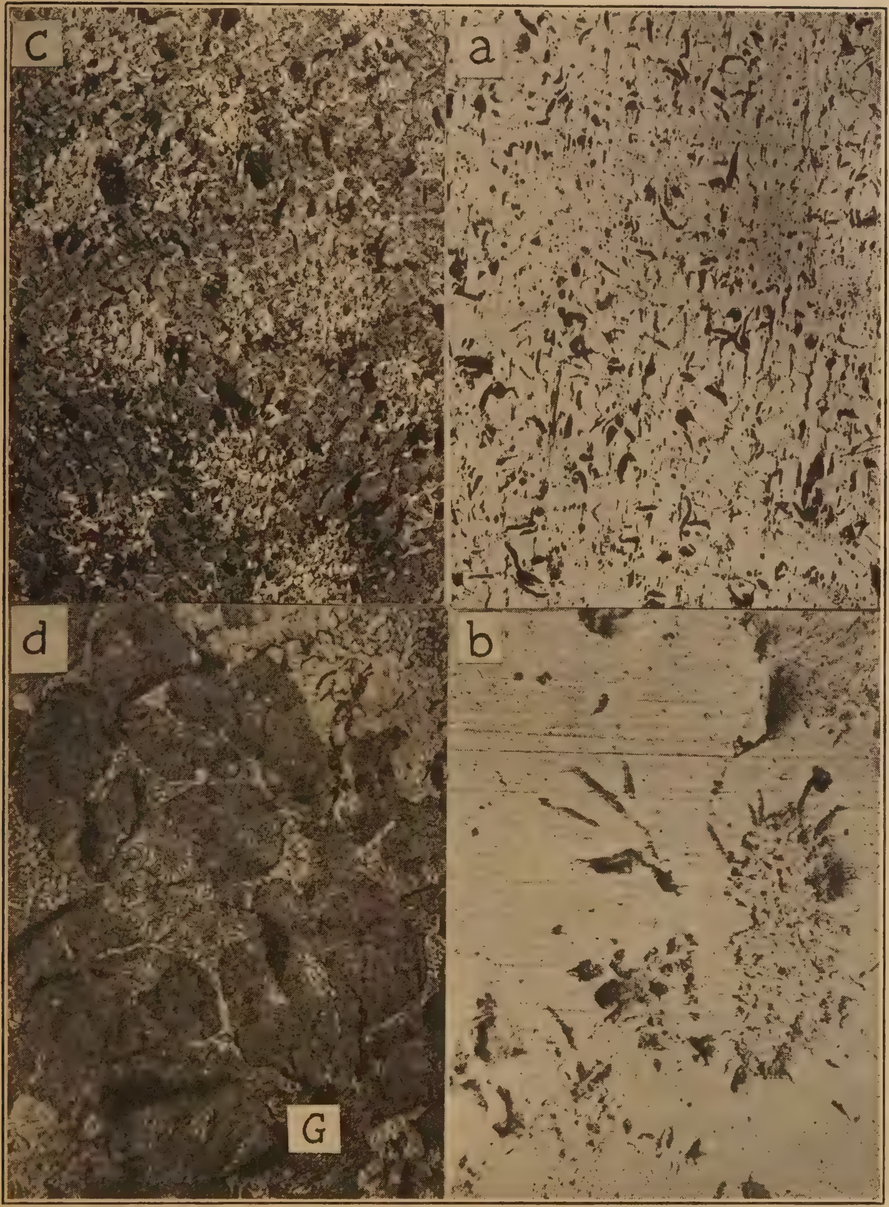
CHEMICAL ANALYSIS BEFORE ENAMELING

	Heat No. 1 %	Heat No. 2 %	Heat No. 3 %
Total carbon	3.40	3.25	3.22
Mn	0.69	0.57	0.44
P	.814	.845	.840
S	.048	.058	.086
Si	2.82	2.77	2.69
Graphitic carbon	3.18	2.84	2.74
Combined carbon	0.22	0.41	0.48

PROXIMATE STRUCTURAL COMPOSITION BEFORE ENAMELING

	Heat No. 1 %	Heat No. 2 %	Heat No. %
Pearlite	27.9	49.6	57.7
Free ferrite	60.7	39.0	31.0
Steadite	8.1	8.45	8.4
Graphite	3.2	2.8	2.7
Mn S	0.1	0.15	0.2

From the chemical analysis it may be seen that the total carbon—and graphite carbon—content is gradually decreasing from the first to the third heat, while the combined carbon content gradually increases. A gradual increase in the sulphur content is to be noticed.



a—Polished. × 100.
b—Polished. × 500.
c—Etched in 5% picric acid. × 100.
d—Etched in 5% picric acid. × 500.
G—Graphite.
Steadite is seen in *d*.

FIG. 3.—Heat No. 3.

Figure 1. *a*, *b*, *c* and *d* show the structure corresponding to heat No. 1 The presence of a large amount of ferrite and some steadite are to be noted. Graphite is shown as round patches composed of very small particles and also in smaller quantity as flakes of larger size.

Specimens of heat No. 2 are represented by Fig. 2, *a* and *b*. An increase in the quantity of pearlite and in the size of graphite particles is to be noticed.

The structure of plates from heat No. 3 is shown in Fig. 3, *a*, *b*, *c* and *d*. A large amount of pearlite and comparatively large sized flakes are found present.

According to the results of enameling test made by the Enameled Metals Section, Ceramic Division, Bureau of Standards (unpublished), there were a number of blisters observed on the enameled[1] iron from heat No. 1, while hardly any were noticed in those from heats Nos. 2 and 3. Thus, if one would base his conclusions on these observations he could state that the quantity of graphite and size of the graphite flakes are of greater importance than the amount of combined carbon in the irons for enameling purposes.

Although there are indications and certain theoretical considerations that a large amount of combined carbon is undesirable in irons used for enameling, this is not evident from the paper discussed above and there are not yet available enough data to warrant such a conclusion. Blistering appears to be a complex phenomenon and there are evidently several factors which might exercise great influence on it. For instance, when working on the theory that carbon is the principal factor which causes blistering one may suppose: (*a*) That the presence of large graphite particles is more desirable than that of the very small particles when the iron to be enameled is treated only by sand blasting and when no preliminary annealing is being employed, for the large particles may be affected more easily by sand blasting and do not burn as readily as the smaller ones do. (*b*) That casting temperatures and rate of cooling which control the amount of combined carbon, the size and shape of graphite particles, the preliminary heat treatment, the temperatures employed, the time of exposure at the high temperature, the extent of the decarburization of the surface to be enameled, etc., must be always borne in mind.

All these considerations suggest problems for the systematic investigations. It would also be desirable to obtain data on enameling tests made on pure as well as on commercial irons and also on steels, white, mottled and malleable cast irons.

The data obtained for the discussion of this paper have been gathered in connection with the investigation of cast iron for the enameling purposes carried on in the Bureau of Standards in coöperation with the Enamel Division of the AMERICAN CERAMIC SOCIETY.

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[1] Wet coat. Ground 900°C—5$^1/_2$ min.; cover 840°C—6 min.

GAS-FIRED ENAMELING FURNACES WITHOUT MUFFLES[1]

By H. H. Clark

ABSTRACT

First attempts to design enameling furnaces reveal unsuccessful results to increase efficiencies. The early attempts to eliminate the undesirable feature of coal-fired furnaces resulted in building furnaces having high thermal heads, uneven heat distribution and which were costly to maintain.

Eventually the intermittent type of enameling furnace was developed. The only possible disadvantage of this type is that speed forks cannot be used.

An example of the installation of a semi-muffle gas-fired enameling furnace in the plant of the Cribben and Sexton Company, Chicago, is cited. Its principal feature is constant atmospheric conditions accomplished by high pressure gas burners. The design, details, performance data and operating costs are given. A résumé stating the many advantages of gas are appended.

Porcelain enameling furnaces for either the sheet steel or cast iron wet process, up to a few years ago, were practically all of the full-muffle type. Most of them used coal for fuel; the coal was fired into the rear end of the furnace. To increase the efficiency higher grade refractories were used in the muffle. However, these refractories did not offset the disadvantages of this type of furnace. To eliminate falling arch tile and uneven heat distribution, a great many other types of furnaces were designed.

Most all of the attempts to build an enameling furnace that would eliminate the undesirable features of the old coal-fired furnaces adhered closely to the original principles of enameling furnace design whether the fuel used was coal or oil. The products of combustion were kept out of the working chamber by a wall of refractory material. This type of furnace requires a high thermal head to drive the heat through the refractory walls. This, of course, results in high maintenance costs as the difference in temperature between the working chamber and the combustion chamber is often as high as 400°F.

Another disadvantage of the old type of furnace was the uneven distribution of heat. When firing a furnace from either the front or rear it is impossible to keep from getting a difference in temperature in the furnace.

To eliminate numerous shut-downs caused by muffle tile breaking or burning out, and to eliminate the unevenness of heat, the intermittent type was designed. A number of these furnaces have been in operation using gas fuel service for the past few years. This intermittent type of furnace has proved to be very satisfactory, largely because it has reduced maintenance costs; it has made even heat distribution possible, and it is possible to burn ware in the presence of a falling temperature. The only possible disadvantage of this type of oven, if any, is that the various speed forks cannot be used.

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[1] Presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, Feb., 1925.

One of these intermittent type furnaces fired with gas has been in operation at the plant of the Cribben and Sexton Company at Chicago for two years. (This concern makes high grade stoves and ranges.) This firm wished to install speed forks on their furnaces. To meet the necessary requirements of speed forks it was decided to build a gas-fired continuous semi-muffle type furnace. The engineers of the Surface Combustion Company together with the coöperation of The Peoples Gas Light & Coke Company of Chicago designed a furnace of this type and installed it in this plant. The principal features of the design are the means adopted to secure constant atmospheric conditions. This was accomplished by using high pressure surface combustion gas burners. These burners give absolute control of the products of combustion. Gas fuel is ideal for this furnace on account of the short flame. This characteristic gives complete combustion under the hearth and only the hot gases ever get into the working chamber.

To get an even distribution of heat, five small burners were placed on each side of the furnace. This gave the same temperature at the door as at the back of the furnace. By having a number of small burners with individual control on each burner and a main control on the gas line, absolute control of heat distribution in the furnace is attained.

The maintenance costs are low on this furnace on account of the elimination of the muffle and the construction of the semi-muffle in its stead. The furnace has a hearth surface of 10 feet deep, 4 feet wide, and the inside height is 2 feet. The hearth and side wall are of carborundum. The outside walls are of 9 inches of fire brick and $13^1/_2$ inches of insulation, all of which is enclosed in a sheet steel case.

This furnace has been in operation for four months and very good results have been secured. This plant is equipped with hand operated forks, two men to a furnace. At the present time a speed fork is being installed and will, of course, show greater production.

Over the period of time this new furnace has been in operation the gas consumption has averaged 1222 cu. ft. per hour of operation which is at the rate of 72 cents per thousand cu. ft. or 88 cents per hour. The work produced has been of sheet steel and the cast iron wet process. The sheet steel varied in gage from number 18 to number 20. The pieces were of sizes varying from $3^1/_2$ sq. ft. to 3 sq. ft. in area; 8 pieces to 100 pieces per load.

The average hourly production has been 531 sq. ft. with hand loading and two men to a furnace. For a few days four men were employed to feed this furnace and the production was increased to 650 sq. ft. per hour, but it was found that the men were in each other's way. But the more pleasing result of this trial run was that the temperatures remained constant no matter how fast the furnace was fed. By operating one gas valve the operators have absolute control over the temperature of the furnace. This can be made automatic, of course, if desired.

On the basis of four months of operation we find that the cost per one-hundred square feet of ware enameled with one coat is 20 cents. This cost is derived as follows:

1222 cu. ft. gas at 72 c. per thousand cubic feet	$0.88
Gas compression expense including power, water, labor	.03
Maintenance	.02
Interest, depreciation, taxes on furnaces and equipment	.14
	$1.07
Average hourly production (sq. ft. of ware enameled)	531

Cost per 100 sq. ft. of ware enameled = $1.07 ÷ 531 = $0.20.

The excellent condition of the furnace after the first four months of continuous operation indicates that its maintenance cost over a long period of time will be practically nothing.

At the present time material is being secured for the purpose of building a similar furnace. This new furnace will be 5 feet wide, 12 feet deep, and 2 feet high (hearth dimensions). This will give a hearth area 50% in excess of the oven formerly mentioned. Tests indicate that gas consumption will be about 10% greater. The reason for this is that the hot gases have a longer travel and the flue gases will consequentially be lower in temperature.

The advantages of the semi-muffle type gas-fired porcelain enameling furnaces are: (1) low maintenance costs, (2) even distribution of heat, (3) absolute control of furnace temperatures, (4) absolute control of furnace atmospheric conditions, (5) superior finished product, (6) low production costs.

TALC AS THE PRINCIPAL BODY INGREDIENT IN VITRIFIED CERAMIC BODIES[1]

By Hobart M. Kraner[2] and Samuel J. McDowell[3]

ABSTRACT

This paper is an attempt to explain the firing behavior of pure talc as well as talc-clay, talc-lime, talc-clay lime, and some other high magnesia mixtures. Phase rule equilibrium diagrams are used. The study applies only to those mixtures where talc is present in amounts greater than 50% of the total composition.

Introduction

Purely theoretical reasoning or the application of theories and data not ordinarily considered ceramic lead often to the solution of many ceramic problems. The firing behavior of steatite (talc), and other high magnesia bodies bonded with clay warrants a study of this sort, and the phase rule diagrams are available for it.

The vitrified products made from such compositions are said to have very desirable characteristics. It is claimed that they possess the highest insulating value of any ceramic material produced at similar temperatures. A low coefficient of expansion, high thermal conductivity, high thermal diffusivity, as well as high dielectric strength is claimed for them.

Pure Talc and Its Melting Behavior

The difficulty in the manufacture of a ceramic product of this type seems to be in controlling its vitrification. The temperature range giving proper vitrification is very narrow and the ware is likely to be either porous from underfiring or bloated and melted from overfiring. On this account it is very difficult to hold the ware to specified dimensions, porosity, or shape. It is said that one manufacturer regularly found it necessary to scrap 60% of his ware. The result is that many steatite products are either fired to a low temperature and left porous, or their manufacture is discontinued.[4]

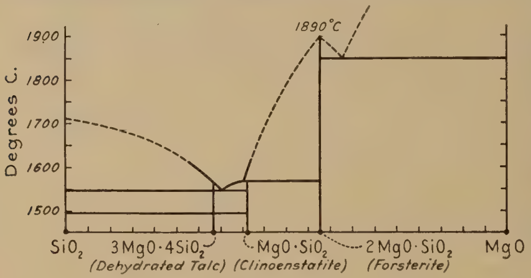

Fig. 1.

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[1] Recd. July 1, 1925.

[2,3] A.-C. Spark Plug Co., Flint, Mich.

[4] Some of the ceramic industry are interested in compositions which are largely talc or other high magnesia minerals bonded with clay. The magnesia mineral in such bodies is the principal ingredient. Deductions made from a body study of this sort cannot therefore be applied to the behavior of other compositions where talc or other high-magnesia mineral is present only in small amount.

Theoretically the molecular composition of pure talc is $3MgO.4SiO_2.H_2O$. Its chemical composition is MgO 31.9, SiO_2 63.3, H_2O 4.8.

It is not likely that many such talcs occur in nature. Dana's system of mineralogy gives the following analyses for selected samples of the mineral:

	SiO_2	FeO	MgO	H_2O	Al_2O_3	NiO	CaO
1	62.12	1.58	31.15	4.73	....	0.24	....
2	61.16	1.40	31.17	5.31	0.46	.39	....
3	60.85	0.09	32.08	4.95	1.71	....	trace
4	62.15	.39	33.04	3.21	1.01	....	0.07
5	61.51	.12	30.93	2.84	0.83	....	3.70
6	62.37	.65	32.02	4.81	.32	....	....
7	60.31	2.11	29.94	5.87	1.24	0.30	....
8	61.69	2.33	30.62	4.94	....	.29	....
9	62.03	1.57	30.62	5.04	0.03	.32	....
10	57.10	1.07	30.11	6.07	5.50	....	....
11	61.51	1.38	30.27	4.88	1.08	1.06	....
12	63.29	4.68	27.13	4.40	1.40	....	trace
13	64.44	1.39	33.19	0.34	0.48	0.23	....
14	57.72	0.64	33.74	6.01	2.52	....	....
15	62.27	.85	30.95	4.91	1.10	....	....

Diller, Fairchild and Larsen[1] give the following compositions:

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	H_2O	
1	61.37	1.96	..	1.47	30.23	none	....	5.36	German
2	61.00	2.12	..	1.74	29.83	none	....	5.56	Indian
3	61.52	0.84	..	1.27	31.38	none	....	5.42	Italian
4	61.94	1.52	..	0.97	31.55	none	....	5.19	French
5	61.35	4.42	..	1.68	26.03	0.82	0.62	5.10	N. Carolina
6	58.68	3.75	..	5.52	26.80	none	....	5.33	Maryland
7	61.00	0.59	..	....	30.84	....	....	5.40	California

If we locate the composition of chemically pure dehydrated talc on the MgO-SiO_2[2] binary diagram as is shown in Fig. 1, it is evident that it is composed largely of the clinoenstatite-silica eutectic composition. Actual calculation shows it to be 95% eutectic composition.

The eutectic melts at 1543°C and eutectic melting is sharp. It is therefore evident that pure talc has practically no firing range and would become fluid almost immediately as soon as that temperature is reached. The excess constituent in this case is 5% silica, but this low percentage of excess solid material would not affect the fluidity of the melt.

Clay and Talc Mixtures

The effect of the addition of clay to talc can be studied on the MgO-Al_2O_3-SiO_2 ternary diagram[3] shown in Fig. 2.

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[1] *Econ. Geol.*, **15**, 574–609 (1920).

[2] N. L. Bowen and Olaf Andersen, "The Binary System MgO–SiO_2," *Amer. Jour. Sci.*, **37**, 478 (1914).

[3] Rankin and Merwin, "The Ternary System MgO–Al_2O_3–SiO_2." *Amer. Jour. Sci.*, **45**, April (1918).

The broken line connecting the compositions $3MgO.4SiO_2$ (dehydrated talc) and $Al_2O_3.2SiO_2$ (dehydrated clay) shows that portion of the field along which mixtures of talc and clay fall. It will be noted that the lowest melting eutectic in the system is nearly on this line, having the composition MgO 20.3, Al_2O_3 18.3, SiO_2 61.4.

This could be compounded from the following:

Raw talc ($3MgO.4SiO_2.H_2O$)	58.1
Raw clay ($Al_2O_3.2H_2O.2H_2O$)	41.5
Alumina (Al_2O_3)	0.4

When ware composed of talc and clay is to be formed by the wet process, the composition necessarily approaches the above eutectic composition very closely. Just how near the eutectic composition it will be, of course, depends upon the exact amount of clay used. Inasmuch as eutectic melting is sharp, there would be very little, if any, sintering preceding the melting at the eutectic temperature. Complete melting occurs at the eutectic temperature. In such a case a few degrees in temperature means the difference between a porous piece of ware and a melted one. This has been proven in practice. Pieces in the same sagger have shown the effect of this small temperature variation. Bonding talc with clay is obviously not to be recommended where the amount of clay is 40% or 50%.

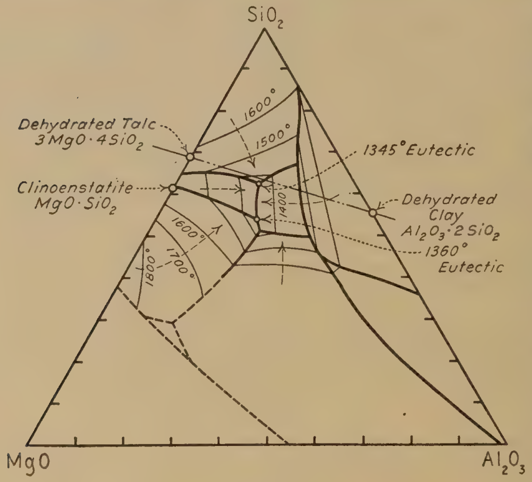

FIG. 2.

Pure Talc in Other Mixtures

Compositions along the broken line (Fig. 2) between the 1345° eutectic and anhydrous talc would be somewhat less difficult to fire, but the theoretical range would still be only that between the melting temperature of the ternary eutectic and the temperature represented by the elevation of these compositions on the surface of the solid diagrams whose slopes are indicated by isotherms and arrows pointing toward the lower temperatures.

Figure 3 shows the position of composition *X* on the $MgO-Al_2O_3-SiO_2$ ternary diagram. In this composition silica (SiO_2) is the crystalline phase in excess of the liquid immediately before melting is complete. This should improve the firing range of the body but the flatness of the field as indicated by the large distance between the isotherms means that a relatively large amount of silica would go into solution in this glass with only small increases of temperature above the eutectic temperature. In some porcelain bodies, the undesirability of the physical properties of the silica minerals would also be a consideration.

Effect of Increase in MgO

From their locations on the ternary diagram, the bodies in the regions thus far considered have either clinoenstatite ($MgO.SiO_2$), or silica (SiO_2), as the primary crystal phase—the last to go into solution upon heating the mixture.

If clinoenstatite is the constituent which contributes valuable properties to these bodies, it is of course necessary to maintain compositions in which it is the excess constituent. If MgO is the most important consideration, other more practical bodies higher in MgO might be considered. Fused MgO and periclase have very high dielectric strengths.[1] It would seem therefore that higher MgO bodies should be considered.

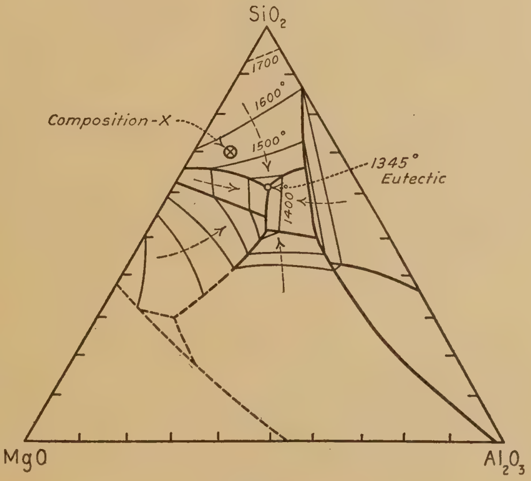

FIG. 3.

A Japanese patent[2] claims that the $MgCO_3$ content of the following mixture is very important in its successful firing.

Talc (raw)	25	Feldspar	10
Talc (calcined)	30	$MgCO_3$	5
Clay	30		

On a basis of phase rule study the real value of only 5% $MgCO_3$ might be questioned. Sufficient MgO addition would, however, place a talc-clay mixture in the forsterite field. It is to be noted that the forsterite field is large, and that the temperature at which the mineral itself melts is relatively high (1890°C) as compared to the melting temperature of the low ternary eutectic (1345°C).

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[1] P. H. Brace, "The Electrical Conductivity of Magnesia and Porcelain at High Temperatures." *Trans. Elec. Chem. Soc.*, p. 205 (1918).

[2] *Ceram. Abs.*, **2**, 199 (1923).

Figure 4 shows composition *Q* lying within the forsterite field of the system forsterite ($2MgO.SiO_2$)–cordierite ($2MgO.2Al_2O_3.5SiO_2$)–spinel ($MgO.$-Al_2O_3), but since the 1360° eutectic is questionably a eutectic,[1] and since in practice the composition would probably not be made up from the minerals mentioned, the 1345° eutectic would be the liquid phase to appear first.

In any system where a compostion is compounded from substances other than the mineral components which would be in equilibrium with each other at an elevated temperature, the lowest eutectic in the system will be the first to form as the temperature is raised.

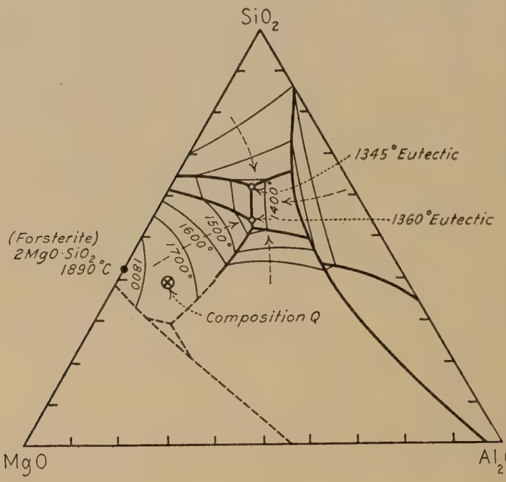

FIG. 4.

In the case of composition *Q* when compounded from $MgCO_3$ (or MgO), talc, and clay, the 1345° eutectic would form first. The stable phases would crystallize from this melt even as the temperature is increased and so long as any of the liquid exists whose composition is located in the distant field.

The forsterite field would seem to have some possibilities so far as a longer firing range is concerned although the compositions on the slope between the clinoenstatite-silica valley and forsterite would feel the effect of the fluid 1345° eutectic as soon as it is formed.

There are practical objections arising to the compounding of mixtures in the forsterite field directly from talc, clay and $MgCO_3$ or MgO. The firing loss in $MgCO_3$ is considerable, and a high shrinkage takes place in the piece when this is used. MgO, even electrically fused, as well as $MgCO_3$ hydrolyzes sufficiently to affect the plasticity of the clay used.

Calcination of the MgO-talc mixture to obtain forsterite ($2MgO.SiO_2$) suggests itself as a means of chemically combining the MgO to prevent its hydrolysis. It must be remembered, however, that this cannot be done completely during calcination unless there is considerable liquid phase present from which the stable phases can crystallize. If the temperature is maintained near or only slightly above that at which this liquid phase remains so, the amount of liquid will decrease to such an extent as to make it mechanically impossible for crystallization to proceed to equilibrium. A temperature considerably higher than the melting point of this first liquid phase should be reached to make combination of the MgO likely. Electric furnace melting suggests itself as the most suitable method.

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[1] Rankin and Merwin, *loc. cit.*

If forsterite as such is bonded with clay, the 1345° eutectic forms first, as before, but the shrinkage is minimized and the range of firing is wider than when talc is used. However, a body of forsterite 70, raw clay 30 would contain about 68% of the 1345° eutectic. This large amount gives little range between the sintering temperature (eutectic temperature) and softening.

Increase of the MgO content beyond the forsterite composition of MgO 57.1, SiO_2 42.9, in an electric furnace product would seem to be the most hopeful possibility inasmuch as the addition of clay to this material would bring the resulting mixture farther from the eutectic area and should lengthen the firing range.

The limiting composition in the addition of MgO in such a fused product is the forsterite-periclase eutectic (see Fig. 1). Mixtures richer in MgO, even after complete fusion, would leave MgO as the excess constituent and therefore free to hydrolyze if given a chance in a ceramic body in the plastic condition. The effect of the hydrolysis would be noted in the workability of the mixture.

Bodies Containing Impurities

Definite information regarding the effect of a few ceramic materials either as impurities or as additions to the batch upon the firing behavior of a pure talc can be obtained from temperature-composition equilibrium diagrams. Unfortunately, the complexity of many ceramic compositions precludes the possibility of diagraming their components and studying their probable firing behavior. We do know, however, that small quantities of many fluxes are conducive to a long firing range. With a large number of fluxes present, the eutectics are complex and their melting temperatures are lower than if the same mixtures were more simple. Inasmuch as the eutectic temperature determines the temperature of sintering, and the percentage of eutectic determines the range between sintering and complete melting, it is possible to exercise a certain amount of control over the firing range.

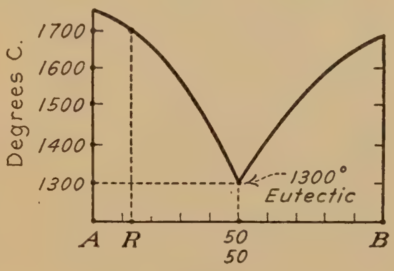

FIG. 5.

Consider Fig. 5. A binary eutectic, 50% A, 50% B, melts at 1300°C.

Composition *R* melts completely at 1700°C. Eutectic or sintering temperature is 1300°C. Range between sintering and melting is 400°C.

Consider Fig. 6. Ternary eutectic, 33.33% A, 33.33% B, 33.33% C, melting at 1100°C. Composition *S* melts completely at 1700°C. Eutectic or sintering temperature is 1100°C. Range between sintering and melting is 600°C.

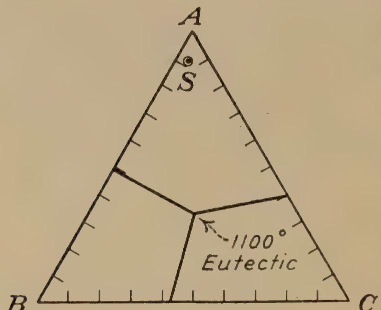

FIG. 6.

From the foregoing it is obvious that it is possible to widen the firing range slightly by increasing the number of constituents, maintaining the refractoriness, or rigidity by decreasing the total amount of these constituents. The impurities in a mineral usually cause a sintering action to take place during firing below the temperature at which chemical action of the theoretically pure mineral should normally take place. For instance, alumina is usually present in an otherwise pure talc. A very small amount of this would permit sintering at 1345°C. See Fig. 2.

Iron bearing impurities are quite common. Unfortunately there are no equilibrium studies available from which we could draw conclusions regarding the behaviors of talc or talc-clay mixtures when these iron-bearing impurities are present. Their presence, however, undoubtedly somewhat lowers the sintering and fusion temperature. This is also true if sodium and potassium bearing minerals are present as impurities.

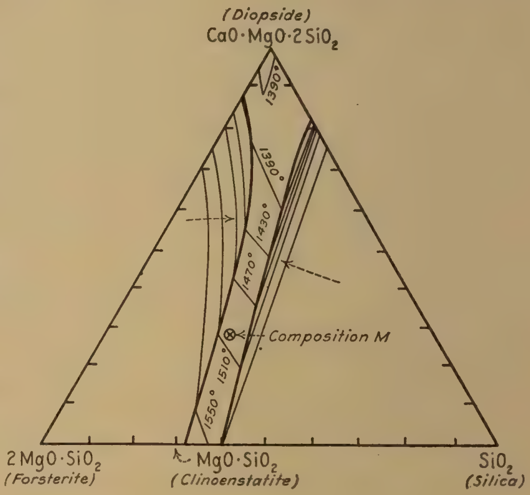

FIG. 7.

The effect of lime (CaO) upon the firing behavior of talc, and clay-talc bodies can be studied in these systems:

Ferguson & Merwin, "The Ternary System Lime–Magnesia–Silica," *Amer. Jour. Sci.*, **48**, 1919.

N. L. Bowen, "The Ternary System Diopside–Forsterite–Silica," *Amer. Jour. Sci.*, **38**, 1914.

Olaf Anderson, "The Ternary System Anorthite–Forsterite–Silica," *Amer. Jour. Sci.*, **39**, 1915.

Tables I and II show no talc containing more than 3.7% CaO. Twells,[1] however, used a commercial talc containing 7% CaO. If this talc were pure otherwise, it would probably have composition of talc 87.5, $CaCO_3$ 12.5, and when fired would analyze MgO 30.89, CaO 7.75, SiO_2 61.35.

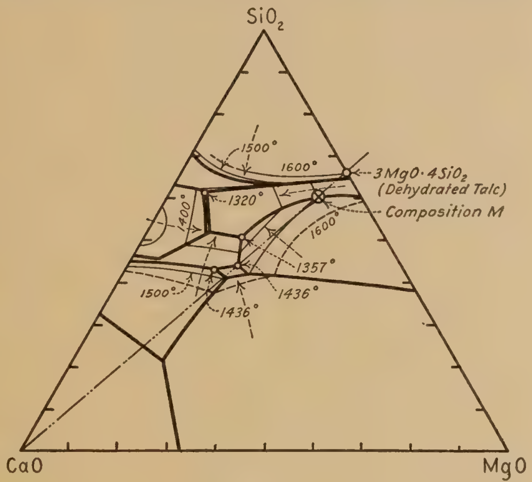

Fig. 8.

The mineral composition of the above after equilibrium had been attained by heating sufficiently, would be diopside ($CaO.MgO.2SiO_2$) 29.9, forsterite ($2MgO.SiO_2$) 44.2, silica (SiO_2) 25.9.

The introduction of CaO through talc into a clay-talc mixture involves a four-component system. For this reason, the low melting mixtures referred to in our use of the anorthite–forsterite–silica system may not be the first to form in the $MgO–CaO–Al_2O_3–SiO_2$ system produced by mixtures of clay, talc and calcium carbonate. The lowest eutectic of the lime–alumina–silica system is itself lower than those in the anorthite–forsterite–silica system. We would therefore expect the eutectics of the $CaO–MgO–Al_2O_3–SiO_2$ system to be even lower than those of the three-component systems. However, since the compositions fall upon the anorthite-forsterite-silica diagram, and there would be some tendency for equilibrium to be established as soon as the four-component eutectic forms during firing, it is probable as firing proceeds that the stable phases of the anorthite–forsterite–silica

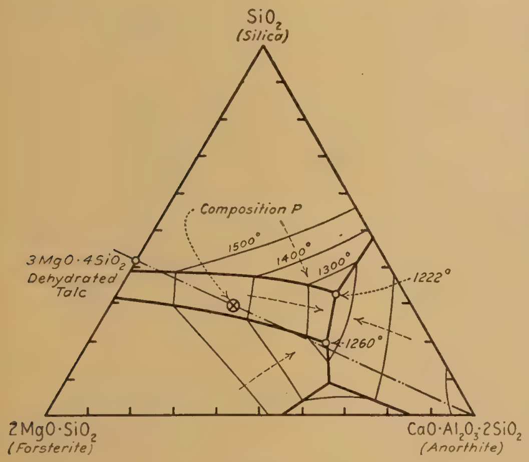

Fig. 9.

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[1] R. Twells, "Further Studies of Porcelain Glazes Maturing at High Temperatures," *Jour. Amer. Ceram. Soc.*, 6 [11], 1113 (1923).

system will crystallize from this first-formed phase. This will place the compositions in the systems indicated.

Figure 7 shows the diopside–forsterite–silica ternary system. The aforementioned talc mixture on this ternary system is designated as composition *M*. The temperature of complete melting of composition *M* is approximately 1500°C, or about 50° less than that of pure talc (see Fig. 1).

Figure 8 shows the ternary system lime–magnesia–silica and composition *M* located on this diagram. Upon heating this material alone, the 1320°C eutectic forms first. This is 180°C between the temperature of first melting and that of complete melting of the mixture. There is 24.21% of the 1320°C eutectic present in this composition and therefore 24.21% liquid as soon as the eutectic temperature is reached. With such a high percentage of fluid one would be led to believe that deformation would soon follow with slight increase of temperature.

If the 7% CaO-bearing talc is bonded with clay in correct proportion the resulting composition could be located on the anorthite-forsterite-silica ternary diagram of Fig. 9. The broken line of this diagram may be considered to represent fired compositions which could be compounded from lime-bearing talcs and clay. It is implied that the clay percentage is such as to keep the lime-alumina ratio as it occurs in anorthite, namely 1:1. The addition of more than this amount of clay will not permit of the study of its effect by the use of this diagram due to the fact that the additional amount of alumina added thereby would throw the composition from the ternary diagram. The addition of only silica would not eliminate it from the diagram and therefore compositions to which it had been added could be studied.

Bonding a 7% CaO talc with clay in suitable amount to place the composition on the broken line gives raw lime-bearing talc 75.6, raw clay 24.4, or after firing, dehydrated talc ($3MgO.4SiO_2$) 70.6, anorthite ($CaO.Al_2O_3.2SiO_2$) 29.4. This is represented by composition *P* of Fig. 9. It begins to melt at 1222°C and passes entirely into a liquid at 1425°C. The high percentage of eutectic present will probably cause deformation soon after the eutectic temperature has been reached.

Summary

It would seem from the foregoing that the prospect of bonding talcs with clay and firing the resulting compositions to vitrification is a doubtful possibility except under particularly good conditions of temperature control. Apparently, however, there seem to be possibilities in compositions lying in the forsterite field. In that field the solubility of forsterite with given increases in temperature is slight as will be noted from the steepness of the slope of the solid model and due also to the high melting point of the mineral itself. The addition of MgO to talc by some suitable method will, of course, effect this change in composition toward the forsterite composition. The least amount of clay which the method of molding will permit will also effect the same improvement in firing behavior by placing the resulting composition closer to that of forsterite.

The presence or addition of small amounts of various RO constituents will also help lengthen the firing range of these bodies.

AN X-RAY STUDY OF CYANITE AND ANDALUSITE[1]

By John T. Norton[2]

ABSTRACT

Samples of cyanite and andalusite have been examined by the X-ray diffraction method, and it has been found that the structures of these two compounds are different from one another and from sillimanite. Upon heating, the compounds are converted into another form which gives the diffraction pattern of mullite or sillimanite.

Sillimanite, cyanite and andalusite are of importance in the ceramic industry because of their conversion on firing to a compound known as mullite or artificial sillimanite. This compound has some very useful properties and the conditions which govern its formation are of interest. Previously,[3] the author has described the X-ray examination of sillimanite which indicated that the artificial compound gave a diffraction pattern which was identical with that of natural sillimanite. It was the purpose of the present investigation to examine cyanite and andalusite in the same way and to determine the temperatures at which the change in structure takes place, provided such a change could be detected.

The arrangement of lines of an X-ray diffraction pattern is characteristic of the material which produces it and in this work the diffraction pattern has been used to identify the principal crystalline constituent of the sample.

Method

The method of obtaining the diffraction patterns was similar to that employed in the previous work on sillimanite. It is the method devised by Hull,[4] and consists in mounting the sample in the form of a fine powder in the path of a monochromatic beam of X-rays, recording the pattern of lines on a photographic film. The method of mounting the samples was improved by grinding with water in a power mortar for several hours, drying, mixing with a binder such as glue or collodion and mounting in a narrow strip on the edge of a card. This procedure resulted in much clearer and sharper patterns than had been obtained before. The process of wet grinding did not introduce any uncertainty as to the composition of the sample because wet and dry ground samples gave exactly the same patterns. By wet grinding, however, it was possible to obtain a sample of the necessary fineness in a much shorter time than by the dry method.

In the cases where the samples were heated, the raw material was ground and placed in a small carbon boat in a carbon tube resistance furnace.

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[1] Recd. Aug. 10, 1925.

[2] Assistant Professor of Physics, Massachusetts Institute of Technology.

[3] Norton, "An X-ray Study of Natural and Artificial Sillimanite," *Jour. Amer. Ceram. Soc.*, **8** [7], 401 (1925).

[4] Hull, "A New Method of X-ray Crystal Analysis," *Phys. Rev.*, **10**, 661 (1917).

The temperature, which was measured with a thermocouple below 1000°C and with a Leeds and Northrup optical pyrometer above, was brought up to the desired point slowly and held there until the sample was heated uniformly throughout. Since the samples were of less than a gram in most cases, this did not require more than a few minutes. The samples were then taken out of the furnace, quenched rapidly in air, ground up with water and mounted. In the neighborhood of the transformation point, the samples were taken out of the furnace every 100°C and it seems certain that the error in measuring the temperature was less than 25°C.

Results

The diffraction patterns obtained from raw cyanite and andalusite are quite different both as regards the position of the various lines and their relative intensity. Upon heating, the patterns which are characteristic of the raw materials are changed, the change, in the case of andalusite, taking place at 1600°C and in the case of cyanite at about 1450°C. The patterns obtained from samples of the two compounds heated above these

TABLE I

SPACINGS OF DIFFRACTION PATTERNS

Andalusite (below 1500°C)		Cyanite (below 1400°C)		Andalusite (above 1700°C)		Cyanite (above 1500°C)	
Spacing (Å. U.)	Intensity	Spacing (Å. U.)	Intensity	Spacing (Å. U.)	Intensity	Spacing (Å. U.)	Intensity
3.45	medium	3.30	strong	3.45	strong	3.45	strong
2.71	strong	3.14	strong	2.90	faint	2.91	faint
2.44	strong						
2.32	very faint	2.95	very faint	2.72	medium	2.72	medium
2.24	strong	2.68	medium	2.56	medium	2.57	medium
2.14	strong	2.50	medium	2.44	faint	2.44	faint
1.95	very faint	2.33	strong	2.30	faint	2.31	faint
1.83	very faint	2.16	faint	2.21	strong	2.22	strong
1.78	medium	1.95	medium	2.13	medium	2.13	medium
1.57	faint	1.91	medium	1.89	very faint	1.89	faint
1.52	medium	1.75	faint	1.84	faint	1.85	faint
1.47	strong	1.66	faint	1.70	medium	1.71	medium
1.38	medium	1.57	faint	1.60	medium	1.60	medium
1.33	very faint	1.50	faint	1.53	strong	1.53	strong
1.28	faint	1.47	faint	1.48	very faint		
1.23	medium	1.37	strong	1.45	very faint	1.45	faint
1.20	faint	1.33	medium	1.40	very faint	1.40	very faint
1.18	faint	1.29	very faint	1.34	faint	1.34	medium
1.07	very faint	1.25	very faint	1.27	faint	1.27	medium
				1.24	faint	1.24	very faint
1.02	faint	1.18	faint	1.19	faint	1.19	faint
		1.09	very faint	1.10	faint		
1.00	faint	1.06	very faint	1.01	very faint	1.10	faint
.98	faint	1.00	very faint			1.01	faint

temperatures were all alike and are identical with the patterns obtained from sillimanite and from the artificial compound which has been called mullite by Bowen and Greig.[1] In the case of cyanite the mullite pattern appears at 1500°C, while in the case of andalusite, the 1600°C sample shows a practically complete set of lines of both patterns and the 1700°C sample shows the mullite pattern alone. In Table I are shown the atomic spacings corresponding to the diffraction lines. Figure 1 shows the diffraction patterns drawn to scale, the height of the line indicating its intensity. These are average values from a number of films. Figure 2 shows some of the actual patterns.

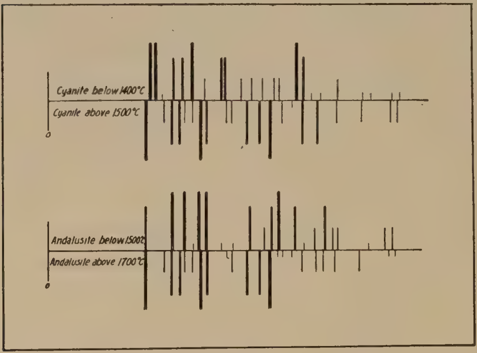

FIG. 1.—Plot to scale of spacings in Table I. The height of the lines is a measure of their intensity.

Conclusions

The X-ray examination of cyanite and andalusite has shown that in the natural form, these two compounds have a different structure, that is, a different arrangement of atoms. It has not been possible from the diffraction patterns to determine the exact arrangement because it is a more or less complicated one but the fact that there is a definite difference in structure is in accord with the results of optical crystallography. The examination also shows that there is a third crystalline form into which

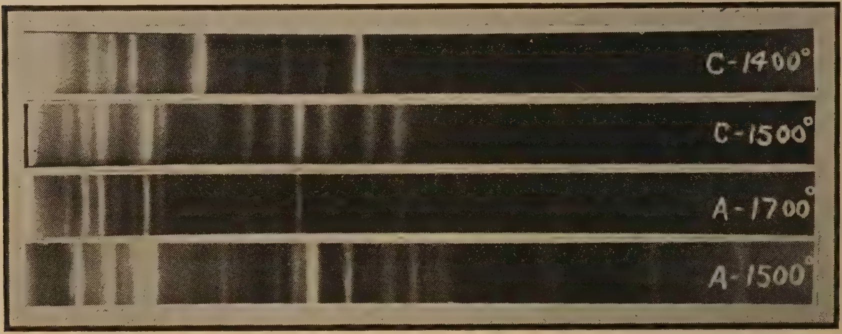

FIG. 2.—Diffraction patterns of andalusite and cyanite showing the change in form.

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[1] Bowen and Greig, "The System Al_2O_3–SiO_2," *Jour. Amer. Ceram. Soc.*, 7 [4], 238 (1924).

cyanite and andalusite can be converted by heating, the cyanite changing between 1400°C and 1500°C and the andalusite between 1500°C and 1700°C. This agrees with the results of Peck[1] except that his conversion temperatures, as measured with cones, are somewhat lower. This third compound gives an X-ray diffraction pattern which is identical with that given by sillimanite and by the artificially prepared compound of alumina and silica which has been called mullite. It does not seem to have been definitely established whether these two compounds are the same or not, but in any case the high temperature form of cyanite and andalusite may be considered the same as the compound formed by heating mixtures of alumina and silica, whatever its name may be. The conclusions may be briefly summarized as follows.

1. Cyanite and andalusite as they occur in nature have different crystal structures.
2. On heating, these two compounds are converted into a third form which is identical with artificial sillimanite.
3. Cyanite is converted at a temperature of about 1450°C and andalusite at 1600°C.

The use of the X-ray diffraction method for identifying the crystalline components of a mixture is becoming quite important, particularly in cases where optical and chemical methods fail to distinguish between dissimilar forms. Since the positions of the diffraction lines are determined by the arrangement of the atoms, the pattern is not affected by accidents in the growth of the crystal. It may be considered as a method of chemical analysis which not only identifies the materials of the compound but also their state of combination. While the method is comparatively new and not very extensively used at present, it is hoped that by applying it to problems of this sort, particularly in cases where there is more or less information from other sources, it may be developed to the point where it can be generally applied.

In conclusion, the writer wishes to acknowledge the kindness of J. L. Gillson of the department of Geology in supplying the samples and the assistance of E. R. C. Ward during the investigation.

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[1] Peck, "Changes in the Constitution and Microstructure of Andalusite, Cyanite and Sillimanite at High Temperatures," *Jour. Amer. Ceram. Soc.*, **8** [7], 407 (1925).

DIFFERENTIATION BETWEEN MULLITE AND SILLIMANITE BY THEIR X-RAY DIFFRACTION PATTERNS[1]

By Louis Navias[2] and Wheeler P. Davey[3]

ABSTRACT

Natural sillimanite, mullite prepared by fusing alumina and silica, and calcined china clays and ball clays have been examined by the X-ray diffraction method. Each photographic film contained on one half the pattern of mullite as the reference substance, and on the other half the pattern of one of the other materials. In this manner direct comparisons of the patterns were made. It is definitely concluded that, while the patterns of sillimanite and mullite resemble each other very closely, there are pronounced differences in the positions of certain lines, especially in the region of 2.12 A to 1.70 A, sufficient for differentiation and identification. It is further concluded that the crystalline phase of highly calcined china clays and ball clays consists of mullite and not of sillimanite.

It is already well known that, although mullite and sillimanite differ considerably from each other in chemical composition, their crystals are very similar, differing mainly in optical properties. Bowen and Greig[4] have described the optical properties of the compound $3Al_2O_3.2SiO_2$ produced artificially in their laboratory by fusing alumina-silica mixtures, while Bowen, Greig and Zies[5] have described the properties of a natural mineral having the composition $3Al_2O_3.2SiO_2$ and termed by them "mullite." The crystals are identical in general chemical composition and in optical properties. The properties as given by these authors are given in Table I. Since the beginning of the year we have been working on the problem of the differentiation between mullite and sillimanite by their X-ray diffraction patterns and have arrived at a positive result. The work has proved all the more interesting because of two recent papers which report a negative result on the same problem.

Table I

Properties of Mullite and Sillimanite

		Mullite	Sillimanite
Crystal system		Orthorhombic	Orthorhombic
Prism angle $(1\ 1\ 0 \wedge 1\ \bar{1}\ 0)$		89° 13′	88° 15′
Cleavage		$\Vert 0\ 1\ 0$	$\Vert 0\ 1\ 0$
Optical orientation		$\bar{c} = \gamma$	$\bar{c} = \gamma$
		$\bar{b} = \alpha$	$\bar{b} = \alpha$
Refractive indices	γ	1.654	1.677
	α	1.642	1.657
Axial angle	2V	+45°−50°	+25°

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[1] Recd. Aug. 15, 1925.

[2] Research Ceramist, Research Laboratory, General Electric Co., Schenectady, N. Y.

[3] Research Physicist, Research Laboratory, General Electric Co., Schenectady, N. Y.

[4] Bowen and Greig, *Jour. Amer. Ceram. Soc.*, **7**, 238–54 (1924).

[5] Bowen, Greig and Zies, *Jour. Wash. Acad. Sci.*, **14**, 183–91 (1924).

Bowen and Greig[1] say "....nor have we found sillimanite in ceramic wares of any kind. The crystals in these are always $3Al_2O_3.2SiO_2$. This observation would seem to be in disagreement with the X-ray analysis of porcelain made by G. Shearer.[2] He subjected natural sillimanite and a piece of porcelain to such analysis using the powder method and obtained identical spectra. However our colleague, Dr. Wyckoff, has kindly made similar powder photographs of our very pure sillimanite from Delaware Co., Pa., and also of the clear, transparent, microscopically homogeneous crystals of $3Al_2O_3.2SiO_2$ and has found that they give identical spectra. This is no place for a discussion of the significance of this observation. Suffice it to say here that the crystals contained in a ceramic ware cannot be established as sillimanite on the basis of X-ray analysis since this method fails to distinguish between that compound and $3Al_2O_3.2SiO_2$."

Norton[3] obtained diffraction patterns of natural sillimanite and of the crystal phase of the calcined products of pure kaolin and of 1:1 and 3:2 alumina and silica mixtures. His conclusions in part are "....As a result of the examination of about 50 films, it has been found that the patterns given by mixtures of pure Al_2O_3 and SiO_2 in the molecular proportions of 3:2 and 1:1 heated to temperatures from 1500° to 1850°C as well as samples of fused kaolin and other pure clays are alike and are identical with the pattern obtained from a sample of natural sillimanite from Norwich, Conn. The agreement was exact both in the position of the lines and in their relative intensities within the experimental error...The conclusion is drawn that the only compound of alumina and silica which is formed under the conditions of these experiments gives an X-ray diffraction pattern which is identical with natural sillimanite." Fortunately, Norton published some of his diffraction data. We have compared his data with ours and believe that we are in a position to point out why he (and probably the same applies to the other workers mentioned) failed to discover differences in the two diffraction patterns.

The Material and Its Preparation

Our sample of sillimanite was kindly loaned to us by Robert B. Sosman of the Geophysical Laboratory. It was originally obtained from Delaware Co., Pa., and constituted part of the sample used and described by Bowen and Greig in their paper.[1] The preparation of mullite by fusing pure silica and alumina in an arc has already been described by one of us.[4] Our sample of mullite was made in this way. In order that there might be no doubt that the sample was really mullite, a portion of the sample was subjected to chemical analysis and its optical properties determined. The results are compared in Table II with Bowen and Greig's results for sillimanite and pure mullite. It is evident, therefore, that our specimens were actually sillimanite and mullite.

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[1] *Loc. cit.*

[2] Bragg, Shearer and Mellor, *Trans. Ceram. Soc.* (Eng.), **22**, 105–10 (1922–3).

[3] Norton, *Jour. Amer. Ceram. Soc.*, **8**, 401–6 (1925).

[4] Navias, *Jour. Amer. Ceram. Soc.*, **8**, 296–302 (1925).

The technique of preparation of specimens for X-ray examination by the "powder method" has already been described by one of us.[1] After grinding, the powdered crystals were sieved through 200-mesh silk bolting cloth in accordance with the regular routine recommended.[1] This insured that the maximum "diameter" of particles was not over .006 cm. The two materials show entirely different characteristics upon grinding. Sillimanite breaks up into prisms whose length is usually about twice the width. It is easy to get particles whose sizes range downward from a maximum of .012 cm. The smaller fragments showed "square" corners. Mullite, ground to the same particle size, breaks up into granular pieces which seem to have no particular cleavage, and which show few real prisms under the microscope. As will be explained later, it was found from the diffraction patterns that the particles of mullite had a tendency to pack together in tiny "lumps" in the specimen tubes. Although the "lumps" themselves had a random orientation, the particles in each "lump" had approximately the same orientation. For this reason some of the mullite was ground to an average diameter of .001 cm. Still another portion was ground wet to an average diameter of about .0002 cm., and then annealed for 2 hours at 900–1000°C to remove any strains caused by grinding. In order to reduce the time of exposure to X-rays in taking the diffraction patterns, every specimen of sillimanite and of mullite was thoroughly mixed with an equal volume of wheat flour.[2] In the case of the finely ground mullite this had the additional advantage of making it more difficult for the crystal fragments to pack together, thus increasing the total number of orientations of crystal fragments in the specimen.

TABLE II

	Bowen and Greig		Navias and Davey
Composition	Sillimanite %	Pure mullite %	Mullite %
SiO_2	37.08	27.60	27.50
Al_2O_3	63.11	73.16	72.13
Fe_2O_3	.09	trace	trace
Refractive indices			
γ	1.677	1.654	1.654
α	1.657	1.642	1.641

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[1] Davey, *Gen. Elec. Rev.*, Aug., 1925.

[2] Because of its transparency to X-rays, the flour reduces the effective opacity of the specimen to the incident and diffracted beams. The flour is so nearly amorphous as to give no appreciable diffraction pattern of its own under the conditions of the experiment.

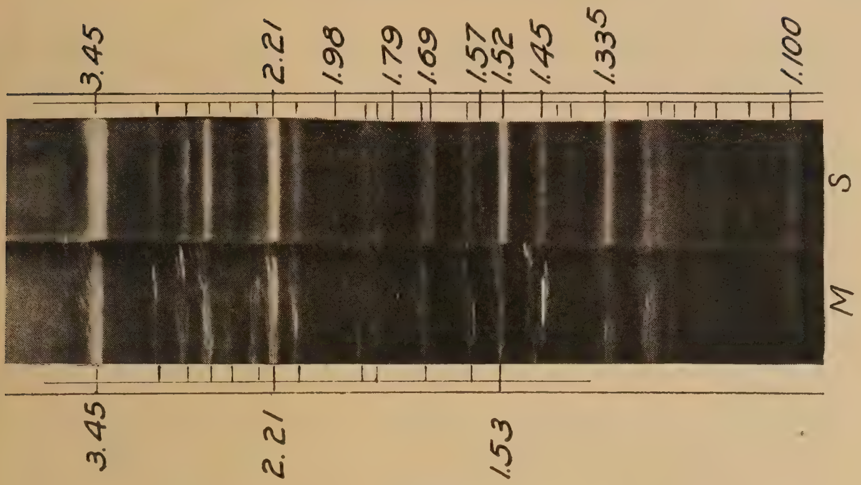

Fig. 1.

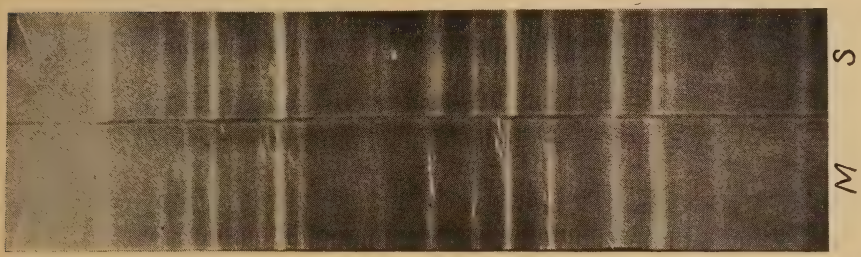

Fig. 2.

Fig. 3.

The Diffraction Patterns

Diffraction patterns of these specimens, three of which are reproduced in this report, were taken on the Standard General Electric Co. X-ray Diffraction Apparatus which has been sufficiently described elsewhere.[1] This apparatus is so designed that the diffraction patterns of two substances may be taken one above the other on the same strip of photographic film. Taking advantage of this design, our specimens were mounted with sillimanite at one end of a glass specimen-tube and mullite at the other end, so that the diffraction pattern of the mullite was always below that of the sillimanite. In this way the two patterns could be compared directly on the same film.

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[1] Davey, *Jour. Opt. Soc. Am.*, **5**, 479 (1921); *Gen. Elec. Rev.*, **25**, 565 (1922).

Figure 1 shows the pattern obtained from the sillimanite and mullite which had been ground to a maximum particle size of .012 cm. and then sieved to give a maximum particle size of .006 cm. It is a matter of ordinary experience in X-ray diffraction work that if the particle size does not exceed .006 cm. the lines of the diffraction pattern are smooth. The pattern of sillimanite in Fig. 1 is in accord with this experience. The pattern of mullite, however, has a scratchy appearance such as is characteristic of particle size considerably in excess of .006 cm. This is explained by assuming that the mullite fragments pack together in lumps such that all the particles in each lump have approximately the same orientation in one plane. Such a packing is already well known for graphite and for iodine. Figure 2 shows the pattern from another portion of the same lot of ground sillimanite (.006 cm. max. diam.) and one from mullite ground to an average size of .001 cm. The mullite lines are still scratchy but not so much as in Fig. 1. Evidently the additional grinding made it possible to produce a more chaotic orientation of the mullite fragments. Figure 3 shows a pattern from a third portion of the same sillimanite as before and a pattern of the mullite which had been ground to an average size of .0002 cm. and then annealed as described above. The mullite lines on this film were as smooth as those from sillimanite. All three films show that most of the lines from the two crystals are identical, but that certain of the lines are considerably different. Additional diffraction patterns were taken, using another diffraction apparatus in which the specimens could be rotated about the axis of the glass specimen-tube. These patterns were identical with those described above, within the experimental error.

In another connection,[1] we have taken diffraction patterns of calcined china clays and ball clays on one half of our photographic films and have simultaneously taken patterns of mullite as a comparison standard on the other half of each of the films. These films have been reviewed, and they indicate again to us that the crystalline phase of the fired clays is mullite, for in every case the pattern from the clay matches line for line with that of mullite.

Discussion of the Diffraction Data

No great precision is claimed for our measurements of the absolute values of interplanar spacings corresponding to each of the lines in the various diffraction patterns described above. Precision measurements of these spacings require the presence, on the same film, of the pattern of a crystal, such as NaCl or calcite, whose structure and lattice parameters are accurately known. It was not our purpose to work out the structure and lattice parameters of either sillimanite or mullite but rather to search for *differences* between their diffraction patterns. For this reason we took the patterns of sillimanite and mullite *on the same film*, thus making it possible to detect *differences* between the two to a high degree of precision. Not having any calibrating pattern on these films, it is not to be expected that the interplanar distances obtained from one film will be identical with those of some other film in our series. It is to be expected, however, that if certain lines of sillimanite and mullite are (within experimental error) identical on one film they will be identical on all the films, and that if certain other lines are different on one film they will be correspondingly different on all the films. That this is actually so is brought out in Table III.[1] Of the other workers in this field, Norton[2] is the only one so far who has published numerical data. We have therefore included his data in our Table III. The published copies of his diffraction patterns are so clear and the number of films he has exposed is so great that we take it for granted that the absolute values of the interplanar distances of sillimanite, published in his article, are much more accurate than any measurements we could make on our films in the absence of a calibration

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[1] Navias, *loc. cit.*

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[1] The slight difference in the diffraction patterns of sillimanite and mullite was to have been expected on theoretical grounds. Table I shows that the prism angles between 1 1 0 and 1 $\bar{1}$ 0 planes of the two crystals differ by about 1°. This means that the axial ratios of the two crystals must be different. The distance L from the zero line (record of the undeviated beam) to any one line in the diffraction pattern is given by $L = \frac{\pi R}{180} \sin^{-1} \frac{n\lambda}{2d}$, where R is the radius of curvature of the film,[3] n is the order of diffraction, λ is the wave-length of X-rays employed and d is the distance between planes which give rise to the line in the diffraction pattern. d may be calculated at once by the ordinary crystallographic formula for the interplanar distance in an orthorhombic crystal,

$$d = \frac{(hx_1 + ky_1 + lz_1) - (hx_2 + ky_2 + lz_2)}{\{(h/A)^2 + k^2 + (l/C)^2\}^{1/2}}$$

where $h\ k\ l$ are the Miller indices of the plane, $x_1y_1z_1$, $x_2y_2z_2$ are the coördinates of successive atoms in the crystal, and A and C are the axial ratios of the crystal. It is evident that slight changes in A and C will make more change in the value of d for some planes (*i. e.*, for some values of $h\ k\ l$) than for others. Therefore the spacing L for the lines in the diffraction pattern will be more affected for some lines than for others. The region on the film where these displaced lines will appear will depend not only on h, k and l but also on $x_1y_1z_1$, $x_2y_2z_2$ and n.

[2] Norton, *loc. cit.*

[3] Davey, *Jour. Opt. Soc. Am.*, **5**, 479 (1921); *Gen. Elec. Rev.*, **25**, 565 (1922).

TABLE III

Navias and Davey							Norton		
Film 1228 (see Fig. 1)		Film 1235 (see Fig. 2)		Film 1282 (see Fig. 3)		Average difference between sillimanite and mullite	Sillimanite	"Artificial compound"	[1] Difference between sillimanite and "artificial compound"
Sillimanite	Mullite	Sillimanite	Mullite	Sillimanite	Mullite				
3.45	3.45	3.45	3.45	3.45	3.45	.00	3.45	3.44	— .01
2.89	2.88	2.92	2.92	2.92	2.92	.00	2.91	2.91	.00
2.69	2.69	2.72	2.71	2.71	2.71	.00	2.69	2.72	+ .03
2.55	2.55	2.57	2.57	2.58	2.57	.00	2.55	2.55	.00
2.43	2.43	2.45	2.45	2.44	2.45	.00	2.43	2.38	— .05
2.30	2.30	2.30	2.31	2.31	2.31	.00	2.30	[a]	[a]
2.21	2.21	2.23	2.22	2.22	2.22	.00	2.21	2.22	+ .01
2.12	2.12	2.13	2.14	2.13	2.13	.00	2.12	2.10	— .02
1.98	[a]	1.99	[a]	1.99	[a]	[a]			
1.87^5	1.89	1.88^5	1.91	1.88	1.91	+ .02			
1.83	1.84^5	1.84	1.85	1.84^5	1.86	+ .01			
1.79	[a]	1.80	[a]	1.80	[a]	[a]			
1.71	1.70^5	1.71^5	1.71	1.71^5	1.71^5	.00	1.70	1.72	+ .02
1.69	[a]	1.69^5	[a]	1.69^5	[a]	[a]			....
1.60	1.59	1.61	1.60	1.60^5	1.60	— .01	1.60	1.61	+ .01
1.57	[a]	1.57^5	[a]	1.57^5	[a]	[a]	1.57	[a]	[a]
1.52	1.53	1.53	1.53	1.52^5	1.53	.00	1.52	1.52	.00
1.45		1.45	1.45	1.45	1.45	.00	1.45	1.45	.00
1.42		1.42^5	[a]			[a]			
1.39^5		1.40	1.41		1.41^5	+ .01?	1.38	1.38	.00
1.33^5		1.33^5	1.33^5	1.33^5	1.33^5	.00	1.33	1.34	+ .01
1.275		1.275	1.270	1.275	1.275	.00	1.27	1.27	.00
1.255		1.255	[a]				1.25	1.24	
1.235		1.235	1.240						
1.210		1.210	[a]						
1.185		1.190	1.190				1.18	1.19	
1.145		1.145	1.145				1.14	1.14	
1.120		1.120	1.120				1.12	1.12	
1.100		1.100	1.100				1.10	1.10	
1.055							1.05	1.04	
1.033									
1.018		1.017	1.018						
1.008		1.007	1.008				1.01	1.01	
.985		.988	.989						

pattern. We have, therefore, adjusted all our readings so that our data for sillimanite correspond closely to Norton's. This was done by sliding the films along in the scale on which interplanar distances were read until one of our lines (the 2.12) matched Norton's reading for the same line, as recorded in his article. This facilitates comparison between his data and ours. Spacings smaller than 1.90 A were determined to the nearest 5 in the third decimal place. It will be noted at once that Norton's data show no lines at all in the region (2.12 A to 1.70 A) where we find our most striking differences between sillimanite and mullite. We are inclined to think that his failure to obtain these lines must have been due to the packing effect mentioned above. Probably grinding to a smaller particle size and longer exposure time would have enabled him to get the additional lines. Since he worked with calcined clays, it is of interest to note that when sufficient exposure was given every one of our diffraction patterns of calcined clays mentioned above shows the characteristic lines of mullite (not of sillimanite) in the region between 2.12 A and 1.70 A. This is consistent with the chemical and optical data of Bowen and Greig.[1]

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[1] Norton gives only the average values of a number of different films. We are therefore unable to tell whether his differences on individual films are as consistent as ours.

[a] A line was found for sillimanite but was not observed for mullite.

Conclusions

(1) We have shown that the X-ray diffraction patterns of pure sillimanite and pure mullite are different.

(2) We have shown by purely X-ray methods that the crystalline component of calcined clays is mullite, not sillimanite. These conclusions are in accord with chemical and optical data to be found in the literature, but are not in accord with the negative results previously reported by several workers in X-ray crystallography.

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[1] Bowen and Greig, *loc. cit.*

THE RELATION OF STRUCTURE AND COMPOSITION TO THERMAL EFFICIENCY OF REFRACTORIES WHEN USED IN REGENERATORS[1]

By Stuart M. Phelps[2]

ABSTRACT

This study shows the relative rates of heat transmission in typical clay, silica, diaspore, fused alumina and silicon carbide refractories, when used as checker brick.

It is shown that by lowering the porosity of checker brick an increase in efficiency is obtained by virtue of its greater heat capacity, which is a function of the weight and specific heat of the material.

The glazing of a clay brick does not appreciably impair its efficiency in regeneration, as is sometimes thought, as shown by experiment and as explained by the fact that the greatest part of the heat leaves the surface of the brick by convection and this is affected only by the surface area, which is not appreciably changed by glazing.

Introduction

There is need of information on the type of fire clay refractories having highest thermal efficiency as regenerator checker brick. Data of this nature on refractories of other compositions is useful, especially when obtained under the same experimental conditions.

Relative Rates of Heat Flow

To calculate thermal efficiencies, it is necessary to determine relative rates of heat flow. A 9-inch brick was heated to a surface temperature of 2300°F and as uniformly throughout as possible. It was then cooled with a constant amount of air passing over it and the temperatures at the surface and center recorded at small time intervals. The mean temperature of the brick at any given time during the cooling was assumed to be the average of the temperatures at the surface and center at that instant. This assumption was necessary since the scope of this investigation could not include the laborious determinations required to give the true mean temperature at any instant during the cooling period. However, this procedure should give relative and essentially accurate information for the various refractories. Using this mean temperature, the specific heat (at this temperature) and the weight of the brick, the relative B.t.u. contents were calculated. In this manner the comparative efficiencies of the refractories when used for regenerators were obtained.

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[1] Presented at the Organization Meeting of the American Refractories Institute held at Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa., April 14, 1925.

[2] Industrial Fellow, Refractories Fellowship, Mellon Institute of Industrial Research.

Equipment and Procedure

A diagram of the furnace used for this work is shown in Fig. 1.

The sample was placed upon checker work. The temperatures were recorded by a potentiometer recorder. The furnace was heated until the surface of the brick was 2300°F and then held at that heat until the temperature of the center of the brick was only slightly below that of the surface. The cooling period was then started by introducing, through the burner pipe, a constant amount of cool air, supplied by a separate motor blower unit. The experimental error of this procedure was small as shown in Fig. 2, where five cooling curves on a single sample of clay brick are plotted.

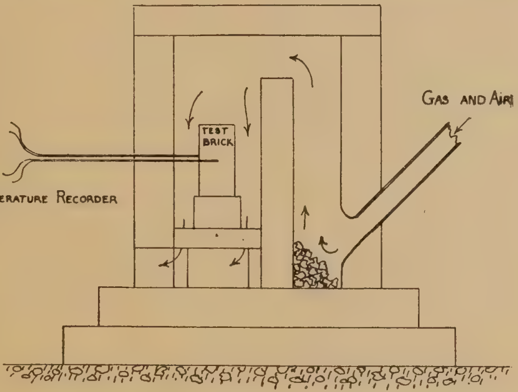

Fig. 1.—Furnace used to study the relative rate of heat flow in refractories.

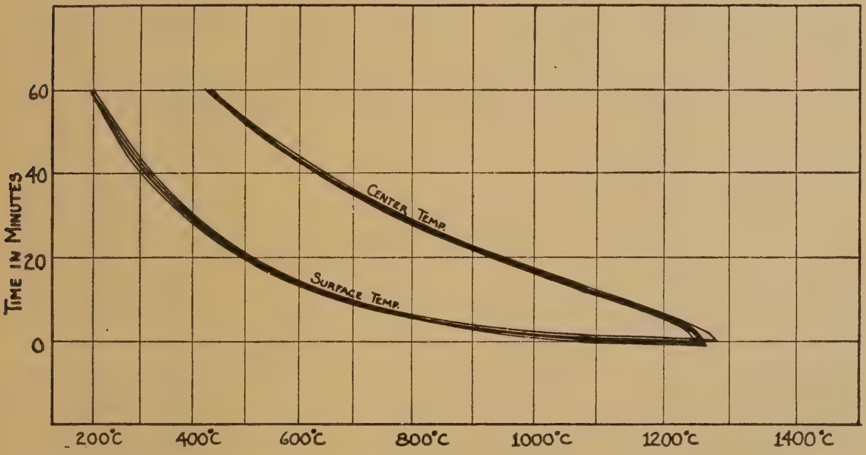

Fig. 2.—Graph showing the experimental error in five runs of a fire clay brick.

Refractories Tested

Some of the properties of the various refractories investigated are given in Table I.

TABLE I

Material	Pounds per cubic foot	Per cent porosity	Silica	Alumina	Lime
A—Clay, low porosity	124.2	13.8	51.68	40.17	
B—Clay, dry pressed	124.4	17.3	50.32	42.95	
C—Clay, high porosity	116.4	25.8	56.28	39.52	
D—Clay, siliceous	113.2	30.5	76.84	19.18	
E—Silica	100.5	27.8	95.20		1.75
F—Diaspore	124.5	36.0	16.60	78.30	
G—Electrically fused alumina	182.0	18.50			
H—Recrystallized silicon carbide	131.2	31.6			

Data Obtained

Cooling Curves

In Fig. 3 the cooling curves for all of the samples tested are plotted. The surface temperatures during cooling show little variation except in the case of silica and silicon carbide. The temperatures at a given time in the center of the several brick show considerable variation due to the different thermal conductivities and different quantities of heat stored in the brick.

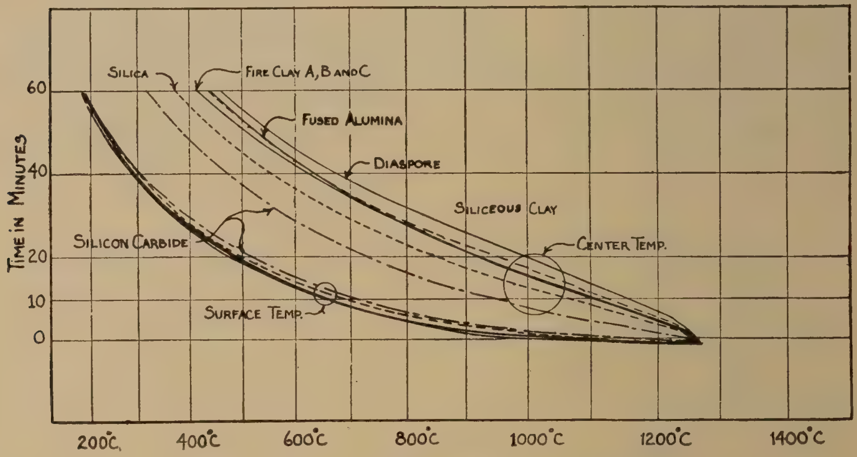

FIG. 3.—Average cooling curves for various brick.

Heat Released on Cooling

The amount of heat contained in a brick at a given temperature is determined by its weight and the specific heat at that temperature. Specific heats for silica and clay refractories have been determined by Bradshaw and Emery,[1] for silicon carbide by O. Weigel,[2] and for fused alumina by Regnault.[3] These specific heats are plotted in Fig. 4. Using these specific heats, and assuming that the siliceous sample *D*, and the diaspore *F*, to be of the same specific heats as silica or clay, and silicon carbide to be approximately 0.08 at 2300°F, the following table of B.t.u.'s given up during the cooling period was calculated from the mean temperatures obtained by the use of the cooling curves shown in Fig. 3. These calculations were made in each case for a single 9-inch brick—9 x 4.5 x 2.5—the results of which are plotted in Fig. 5 and are presented in Table II.

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[1] Bradshaw and Emery, *Trans. Ceram. Soc.* (Eng.), **19**, 88 (1919–20).

[2] O. Weigel, "Treatise on Inorganic Chemistry," J. W. Mellor, vol. **5**, p. 880.

[3] Regnault, Landolt Boernstein.

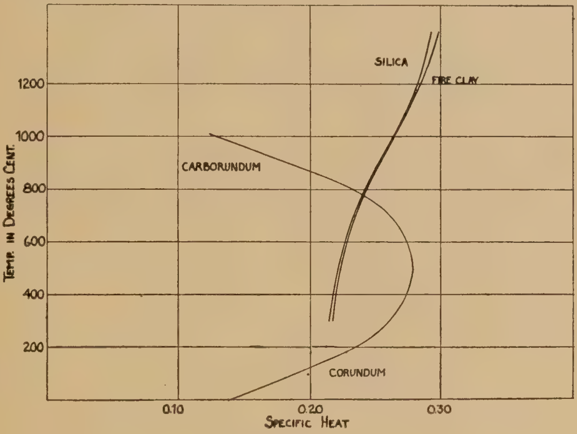

FIG. 4.

There is a considerable difference in the amounts of heat given up by the various brick during cooling, as shown by these data. Such difference in efficiency would be very important in a practical installation using hundreds of such brick as checkers. This difference in efficiency is due, principally, to the different quantities of heat that can be stored in a given volume of the refractories and the speed at which it can be conducted to the surface.

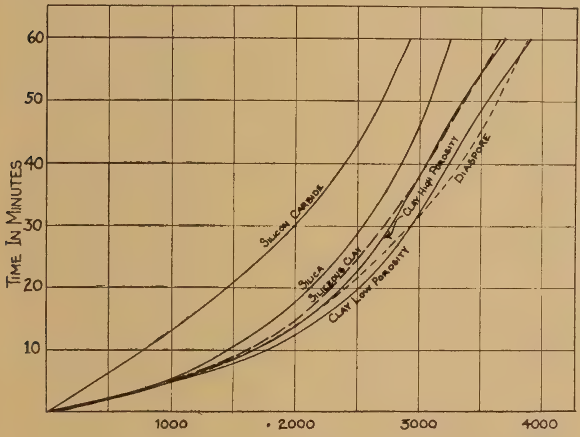

FIG. 5.—B.t.u.'s per brick given up during cooling.

Comparing the three clay samples *A*, *B* and *C*, it will be noted that sample *B* has the greatest weight per brick, *A* coming next and *C* the lowest. As the specific heat of these clay brick is the same, it is evident that for a given temperature the B.t.u.'s held by these materials will be of the same order as their bulk density. Furthermore, as the cooling curves for all three clay bricks were identical, this same order holds for B.t.u.'s given up during cooling. During a given period *A* or *B* give up a greater quantity

TABLE II

Material	Pounds per brick	B.t.u.'s in the brick at 1260°C (2300°F)	Temperature and B.t.u.'s given up during cooling from 1260°C (2300°F)			
			10 Min.	20 Min.	40 Min.	60 Min.
A—Clay, low porosity	7.33	4840	885° C(1625°F) 1740	702°C (1295°F) 2510	505°C (941°F) 3245	300° C (572°F) 3935
B—Dry-pressed clay, medium porosity	7.35	4860	885°C (1625°F) 1760	702°C (1295°F) 2530	505°C (941°F) 3264	300°C (572°F) 3956
C—Clay, high porosity	6.87	4540	885°C (1625°F) 1640	702°C (1295°F) 2360	505°C (941°F) 3050	300°C (572°F) 3700
D—Clay, siliceous	6.88	4550	895° C(1643°F) 1600	717°C (1322°F) 2270	505°C (941°F) 3050	315°C (600°F) 3660
E—Silica	5.93	3920	865°C (1589°F) 1480	675°C (1247°F) 2120	425°C (797°F) 2850	280°C (536°F) 3240
F—Diaspore	7.35	4850[1]	910°C (1670°F) 1650[1]	735°C (1355°F) 2380[1]	490°C (914°F) 3310[1]	320°C (608°F) 3880[1]
H—Recrystallized silicon carbide	7.74	3630	825°C (1517°F) 750	625°C (1127°F) 1480	385°C (725°F) 2400	252°C (485°F) 2910

[1] Calculations made by assuming the specific heat of diaspore to be the same as that of clay.

The data given above are for a 9 x $4\frac{1}{2}$ x $2\frac{1}{2}$-inch brick in each case.

of heat than *C*, which can occur only by virtue of a higher thermal conductivity in the case of *A* or *B*. Such a difference in heat transfer may be explained by the findings of A. T. Green,[1] who has shown that pores of a certain size act, within a given temperature range, as insulators. This subject is also discussed by Calvert and Caldwell.[2]

Glazed Surface of Checker Brick Not Detrimental

An interesting experiment was conducted with the high porosity brick *C*, in which the brick was completely glazed in such a manner as to give a thin, smooth, glassy surface. On comparing the cooling curves of this brick in its original condition, and after being glazed, it was found that they were identical. This is to be expected, since a very large quantity of the heat was given up by convection from the surface of the brick. The function of convection is not appreciably affected under such conditions by changing the nature of the surface of the brick by glazing it, since the surface film is substantially of the same area before and after glazing. Accordingly, it may be assumed that the glazing of checkers in a regenerator does not impair their thermal efficiency.

Comparison of Silica and Clay as Checkers

The siliceous clay sample *D* is a somewhat less efficient checker brick than the clay bricks *A* or *B*, the explanation of which may be, as pointed out above, the high porosity of this material.

Rapid cooling is shown by the curve obtained from the silica brick *E*, which is to be expected in view of the comparatively small number of B.t.u.'s stored in this brick at 2300°F and the relatively high thermal conductivity attributed to it by practical men. By reason of their low bulk density, silica brick have a comparatively small heat capacity, thus making them less suitable for checker brick than clay brick.

No information is available regarding the specific heats of diaspore, so little can be said regarding sample *F*. However, with its high porosity and lagging cooling curve, it might be expected that this material has a low thermal conductivity, provided its specific heat is approximately that of clay.

Specific heats for electrically fused alumina have not been determined at high temperatures and the order of its thermal conductivity is a matter of controversy, so nothing definite can be said regarding the behavior of this refractory in regenerators. This material has approximately the same specific heat at 100°C as that of clay, and, provided it follows the same characteristic as clay at higher temperatures, it would make an efficient checker brick, as its cooling curve is substantially that of clay, but possesses a very high bulk density, allowing it to store a greater quantity of heat.

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[1] A. T. Green, *Gas J.*, Supp., July 9 (1925).

[2] Calvert and Caldwell, *Ind. Eng. Chem.*, **16** [5], 483 (1924).

Silicon Carbide of Little Value for Checkers

Recrystallized silicon carbide possesses a high thermal conductivity and a low specific heat. By virtue of this high conductivity, this material cooled rapidly, especially as it contained a relatively small quantity of heat to be dissipated. For checker work, brick of this composition would be of little value, except in an operation where rapid reversal of the regenerators would be desirable.

Summary

1. The usefulness of fundamental data, such as the specific heats of fused alumina and diaspore at high temperatures, is evident.
2. Silicon carbide possesses a combination of high thermal conductivity, but low thermal capacity.
3. Silica brick have, by virtue of their low apparent density, a low thermal capacity, making them less suitable for checkers than clay brick.
4. Great differences in regenerator efficiency can be had by the use of clay brick of varying porosity. The denser the brick, the more efficient it is in checker work operation. Fortunately such brick are more resistant to slag action than those of more open structure, have less shrinkage in service, and do not deform under load as readily.

Acknowledgment

The author wishes to thank M. C. Booze for the helpful suggestions given during this investigation.

THE CHEMICAL AND PHYSICAL PROPERTIES OF FIRE CLAYS FROM VARIOUS PRODUCING DISTRICTS[1]

By M. C. Booze[2]

ABSTRACT

The chemical analyses, fusion points and firing characteristics of a number of flint and plastic clays from various districts are given, together with a short discussion of the results and the use which can be made of them.

Clays were tested for chemical composition, fusion point, drying and firing shrinkage, and fired porosity. The methods of tests given in the 1922 report of the American Ceramic Society Committee on Standards were closely followed in each case, except that the dry volumes of the test pieces were determined according to the method recommended by Crawford.[3]

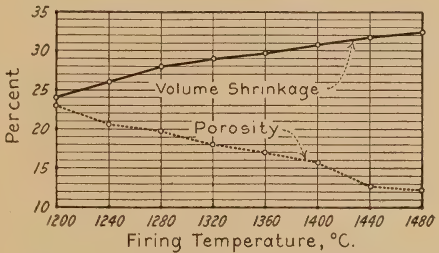

Fig. 1.—Firing characteristics. Raw smooth flint clay, Missouri. Fusion point, cones 32–33.

Both the flint and plastic clays may be divided into open and dense firing groups. A further classification of the dense burning plastic clays is possible by separating those which overfire from those which do not. The property of overfiring is largely limited to the plastic clays, only one of the flint clays (Fig. 25) giving evidence of this and then not to a pronounced degree.

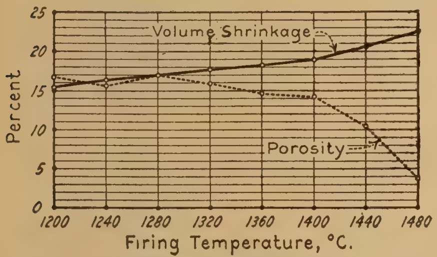

Fig. 2.—Firing characteristics. Raw Cheltenham clay, Missouri. Fusion point, cones 30–31.

There is no relation between chemical composition or fusion point and the property of being open or dense burning. The two most open burning plastic clays (Figs. 16 and 19) have silica contents of 44% and 76%, and fusion points of cones 32–33 and cone 30, respectively, while the plastic clays which burn dense and then overfire vary within almost the same limits. The

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[1] Presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, Feb., 1925.

[2] Senior Industrial Fellow, Multiple Industrial Fellowship of the Refractories Manufacturers Association, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

[3] "A Simplified Method of Determining the Dry Volumes of Clay Briquettes," *Jour. Amer. Ceram. Soc.*, **5**, 394 (1922).

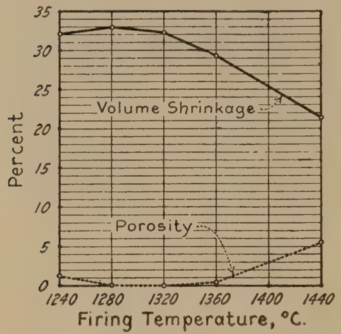


FIG. 3.—Firing characteristics. Raw plastic clay (B 291), Missouri. Fusion point, cone 32.

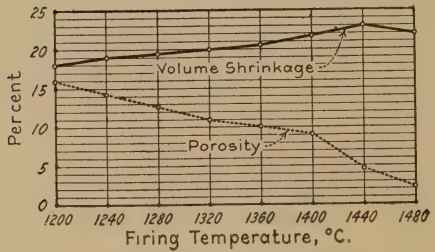


FIG. 4.—Firing characteristics. Select crude pot clay, Missouri. Fusion point, cones 30–31.

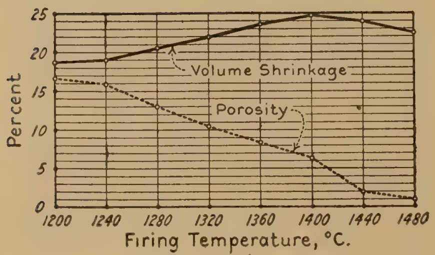


FIG. 5.—Firing characteristics. Raw plastic clay (No. 118), Missouri. Fusion point, cone 31.

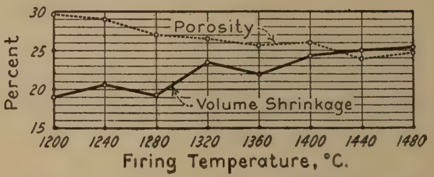


FIG. 6.—Firing characteristics. Raw Burley flint clay, Missouri. Fusion point above cone 33.

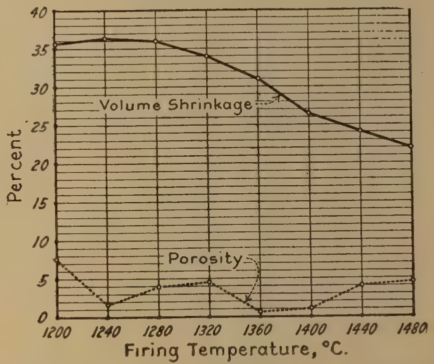


FIG. 7.—Firing characteristics. Plastic bond clay, Maryland. Fusion point, cones 31–32.

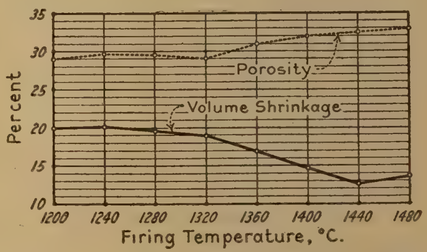


FIG. 8.—Firing characteristics. Flint clay, Maryland. Fusion point, cones 33–34.

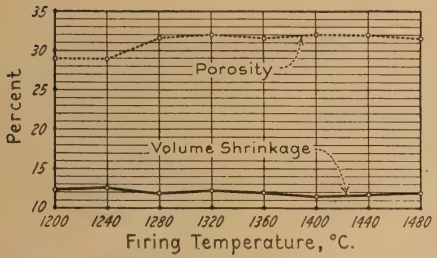


FIG. 9.—Firing characteristics. Flint clays, Colorado. Fusion point, cone 32.

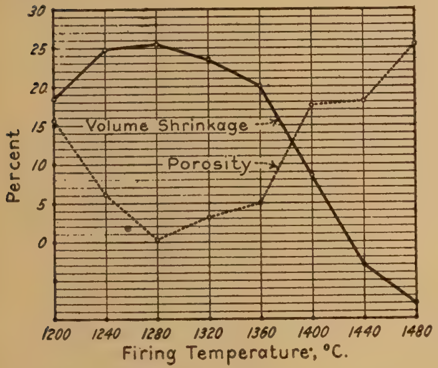


FIG. 10.—Firing characteristics. Plastic clay, Colorado. Fusion point, cone 27.

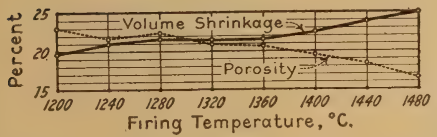


FIG. 11.—Firing characteristics. Semi-flint clay, Colorado. Fusion point, cone 32.

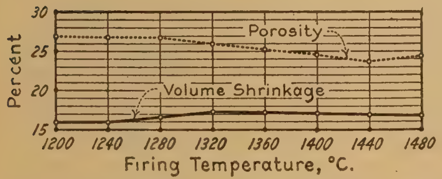


FIG. 12.—Firing characteristics. Dean flint clay, Pennsylvania. Fusion point, cones 33–34.

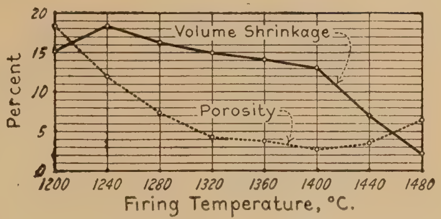


FIG. 13.—Firing characteristics. Plastic clay, Westmoreland County, Pennsylvania. Fusion point, cones 30–31.

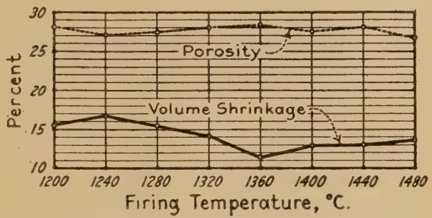


FIG. 14.—Firing characteristics. Flint clay, Clinton County, Pennsylvania.

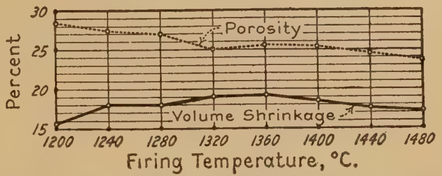


FIG. 15.—Firing characteristics. Monument flint clay, Pennsylvania. Fusion point, cones 32–33.

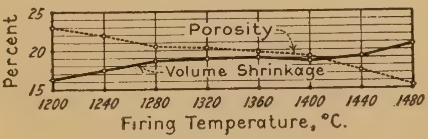


FIG. 16.—Firing characteristics. Plastic bond clay, Cambria County, Pa. Fusion point, cones 32–33.

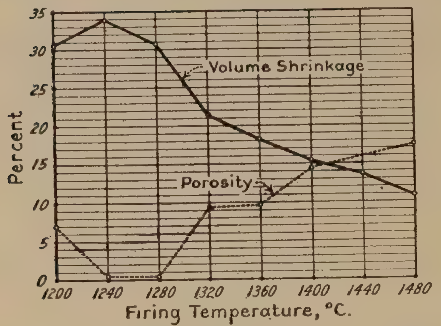


FIG. 17.—Firing characteristics. Rockingham plastic clay, New Jersey. Fusion point, cones 27–28.

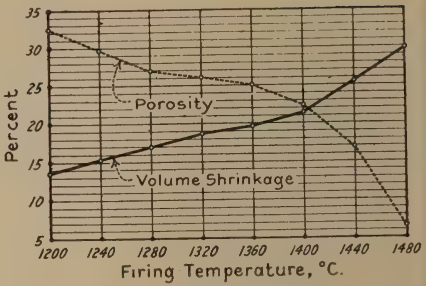


FIG. 20.—Firing characteristics. Plastic clay No. 32, New Jersey. Fusion point, cone 30.

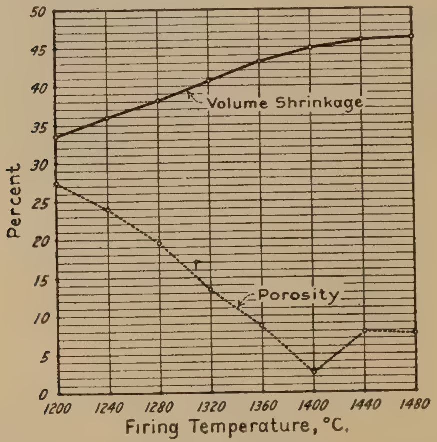


FIG. 18.—Firing characteristics. No. 1 fine clay, New Jersey. Fusion point above cone 33.

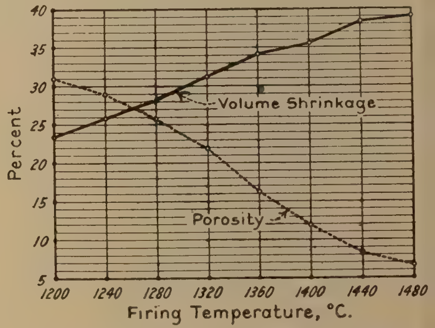


FIG. 21.—Firing characteristics. No. 2 fine clay, New Jersey. Fusion point, cones 32–33.

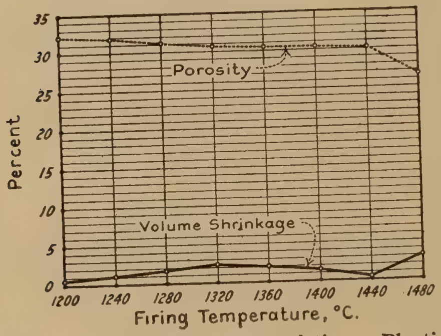


FIG. 19.—Firing characteristics. Plastic clay No. 38, New Jersey. Fusion point, cone 30.

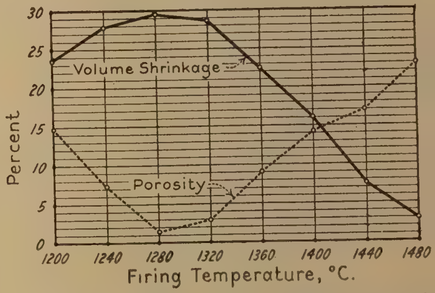


FIG. 22.—Firing characteristics. Plastic clay No. 30, New Jersey. Fusion point, cone 30.

clays in this latter group are also characterized by minimum porosities which are equal to zero in almost every case, and by comparatively high alkali contents; the range in the latter being from 0.97% to 2.60%, with an average of 1.58%, while the dense firing plastic clays which do not overfire vary from 0.12% to 0.49% with an average of 0.32%. An exception to this is the clay shown in Fig. 16, which is open firing and has an alkali content of 1.57%. The alkalis appear to have a very pronounced effect upon both the fusion point and the firing properties. An increase or decrease of $^{1}/_{2}$% in a clay which is otherwise uniform can usually be detected by a change in the fusion point.

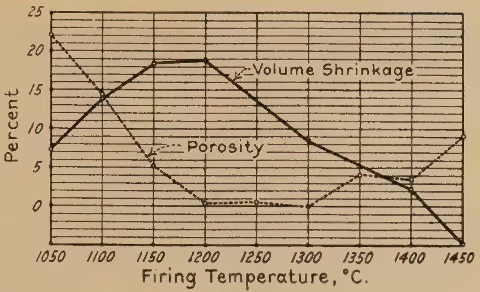


FIG. 23.—Firing characteristics. Black plastic clay, Kentucky. Fusion point, cones 20–26.

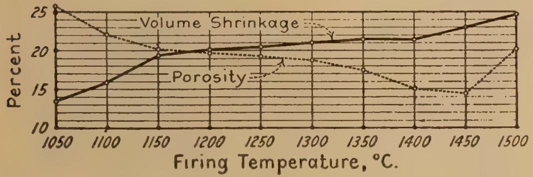


FIG. 24.—Firing characteristics. Hard semi-flint clay, Kentucky. Fusion point, cones 32–33.

As compared to the plastic clays, all of the flint clays are open burning. This may be due as much to the fact that they are not slaked down by water to a fine grain size as to their relative degree of purity. Fineness of grain in itself has an influence upon firing density as has been determined on materials entirely lacking in the plastic properties of clays. Aside from this, the flint clays are also lacking in the cohesiveness possessed by plastic materials which aids in consolidation.

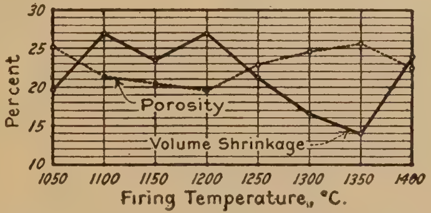


FIG. 25.—Firing characteristics. Flint clay, Kentucky. Fusion point, cone 32.

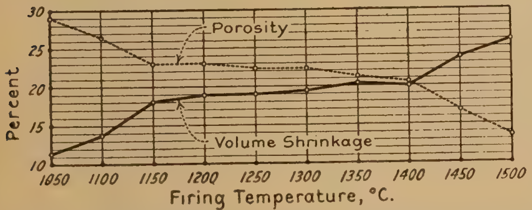


FIG. 26.—Firing characteristics. Soft semi-flint, Kentucky. Fusion point, cones 32–33.

It is difficult to make comparisons between various districts in the quality of their clays as there are no outstanding differences which separate them. The Missouri district is generally credited with clays of higher alumina content than the other districts, but the difference is largely in amounts of these clays available. The burley flint clay of Missouri on which results are given here is matched by nodular flint clay from Pennsylvania and a high alumina flint from Kentucky.

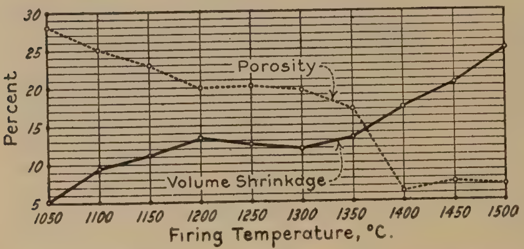
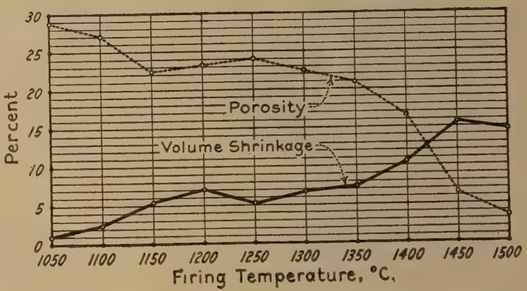


FIG. 27.—Firing characteristics. "Pink eye" plastic clay, Kentucky. Fusion point, cones 20–26.

While the New Jersey district produces no flint clay, it has a great variety of refractory materials. It is commonly supposed that all of the clays from this locality are highly siliceous, but the analyses of the No. 1 and No. 2 "fine" clays show the error of this assumption. The bulk of the refractory clays which are used in this state are low in their content of fluxes and the products owe their good load carrying capacity to this fact as much as to the incorporation of siliceous clays with the plastic bond clays.



FIG' 28.—Firing characteristics. Siliceous semi-flint clay, Kentucky. Fusion point, cones 29–30.

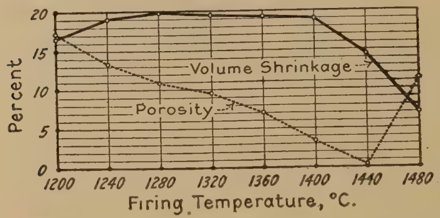


FIG. 29.—Firing characteristics. Plastic clay, southern Ohio. Fusion point, cone 28–29.

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Acknowledgment

As this paper is very largely a record of tests, the credit for it is due the various members of the laboratory staff who obtained the extensive amount of data which was necessary.

Chemical Analyses and Firing Properties of Fire Clays from Various Producing Districts

MISSOURI DISTRICT

Chemical analysis	Raw smooth flint clay	Raw Cheltenham clay	Raw plastic clay (B-291)	Select crude pot clay	Raw plastic clay (No. 118)	Raw burley flint clay
Ignition loss	13.86	11.96	12.10	12.04	11.26	13.30
Silica	43.32	54.78	49.62	55.04	53.12	34.62
Alumina	39.35	28.84	33.15	28.75	31.16	48.03
Iron oxide	0.77	1.98	1.55	1.55	1.18	1.09
Titania	2.00	1.64	1.56	1.68	1.76	2.28
Lime	0.16	0.43	0.13	0.42	0.12	0.25
Magnesia	.33	.72	.93	.80	.48	.56
Alkalis	.22	.21	.97	.48	.49	.44
Total	100.01	100.56	100.01	100.76	99.57	100.57
Fusion point Cone	32–33	30–31	32	30–31	31	Above 33
Burning properties						
Water of plasticity	19.78	21.2	32.5	22.3	17.86	23.3
Drying shrinkage	9.3	22.3	32.1	25.6	14.09	11.4
Av. firing shrinkage						
1200°C	23.9	15.4	....	17.9	18.6	19.2
1240	26.2	16.2	32.7	19.1	18.9	20.6
1280	27.8	17.3	33.2	19.5	20.7	19.3
1320	29.3	17.8	32.4	20.0	22.1	23.5
1360	29.6	18.3	29.4	20.4	23.6	22.1
1400	30.8	19.0	Blew up	21.6	24.7	24.4
1440	31.6	20.8	21.85	23.2	24.2	24.9
1480	32.2	22.7	....	22.0	22.5	25.2
Av. porosity						
1200°C	23.1	16.7	....	15.9	16.6	29.7
1240	20.6	15.8	1.4	14.4	15.8	29.2
1280	19.6	17.3	0.25	12.6	13.3	27.0
1320	18.1	16.0	.3 exp.	11.0	10.5	26.6
1360	17.2	14.7	.46	10.1	8.4	25.9
1400	15.8	14.3	Blew up	9.1	6.3	26.0
1440	14.2	10.6	5.9	4.5	2.0	24.3
1480	13.9	4.0	....	2.3	1.1	25.1

CHEMICAL ANALYSES AND FIRING PROPERTIES OF FIRE CLAYS FROM VARIOUS PRODUCING DISTRICTS

	MARYLAND DISTRICT			COLORADO DISTRICT	
Chemical analysis	Plastic clay	Flint clay	Flint clay	Plastic clay	Semi-flint clay
Ignition loss	9.02	14.60	12.24	6.16	14.16
Silica	52.88	42.76	54.06	70.82	49.02
Alumina	33.61	39.15	32.05	19.43	34.78
Iron oxide	1.63	1.11	0.49	1.03	0.72
Titania	1.28	2.80	1.00	0.84	.96
Lime	0.22	0.18	0.43	.18	.39
Magnesia	.49	Trace	.25	.44	.24
Alkalis	1.39	0.23	.12	1.37	.37
Total	100.52	100.83	100.64	100.27	100.64
Fusion point Cone	31–32	33–34	32	27	32
Burning properties					
Water of plasticity	34.1	17.4	20.7	25.6	20.0
Drying shrinkage	24.8	7.3	11.1	19.3	15.0
Av. firing shrinkage					
1200°C	35.6	20.0	12.4	18.8	19.7
1240	36.4	20.1	12.8	24.9	21.1
1280	35.9	19.6	12.0	25.6	21.7
1320	34.0	19.3	12.5	23.5	21.6
1360	30.9	17.3	12.0	20.1	21.7
1400	26.3	14.6	11.6	8.7	22.5
1440	24.0	12.7	11.7	3.1 exp.	24.0
1480	22.2	13.6	12.3	8.2 exp.	25.1
Av. porosity					
1200°C	7.6	28.9	29.1	15.6	23.0
1240	1.6	29.7	28.9	6.3	21.5
1280	3.9	29.5	31.9	0.37	22.4
1320	4.8	29.1	32.0	3.3	21.0
1360	0.7	30.9	31.6	5.1	20.5
1400	1.1	32.0	32.1	17.5	19.7
1440	4.1	32.5	32.0	18.2	18.4
1480	4.5	33.0	31.6	25.5	16.7

CHEMICAL ANALYSES AND FIRING PROPERTIES OF FIRE CLAYS FROM VARIOUS PRODUCING DISTRICTS

	KENTUCKY DISTRICT					
Chemical analysis	Siliceous semi-flint clay	Soft semi-flint clay	Hard semi-flint clay	Black plastic clay	Flint clay	"Pink-eye" clay
Ignition loss	8.86	14.40	14.08	9.66	13.60	9.36
Silica	65.04	46.16	43.46	55.92	41.00	57.36
Alumina	22.29	35.04	37.45	24.71	37.22	24.85
Iron oxide	1.13	1.42	1.19	4.79	5.78	5.95

Titania	1.60	2.44	2.80	1.52	2.00	1.64
Lime	0.21	0.27	0.30	0.34	0.25	0.15
Magnesia	.47	.49	.64	1.01	.46	.71
Alkalis	1.38	.64	.93	1.57	.42	.37
Total	100.98	100.86	100.85	99.52	100.73	100.39
Fusion point Cone	29–30	32–33	32–33	20–26	32	20–26
Firing properties						
Water of plasticity	13.9	16.8	14.6	18.9	17.5	17.4
Drying shrinkage	11.9	13.0	10.8	18.8	3.0	12.8
Av. firing shrinkage						
1050°C	1.1	11.5	13.5	7.7	19.7	5.2
1100	2.6	13.7	16.1	14.0	27.0	9.8
1150	5.6	18.2	19.5	18.5	23.7	11.2
1200	7.0	19.1	20.2	18.8	27.0	13.5
1250	5.3	19.1	20.5	....	21.3	12.8
1300	6.9	19.6	21.2	8.5	16.8	12.1
1350	7.6	20.6	21.7	....	14.0	13.7
1400	10.8	20.1	22.4	2.4	27.4	17.6
1450	15.6	23.9	23.1	5.3exp.	....	20.4
1500	14.7	26.0	24.8	....	....	25.0
Av. porosity						
1050°C	28.9	29.0	25.8	22.2	25.3	28.0
1100	27.3	26.6	22.3	14.2	21.4	25.0
1150	22.8	23.3	20.0	5.3	20.4	23.1
1200	23.3	23.4	19.9	0.6	19.5	20.0
1250	24.1	22.6	19.4	.7	22.9	20.2
1300	22.8	22.5	18.7	....	24.9	19.8
1350	21.0	21.4	17.5	4.3	25.9	17.1
1400	16.7	20.5	15.0	3.6	19.3	6.5
1450	6.8	16.9	14.4	9.1	....	7.5
1500	3.7	13.5	13.5	....	....	5.4

CHEMICAL ANALYSES AND FIRING PROPERTIES OF FIRE CLAYS FROM VARIOUS PRODUCING DISTRICTS

	NEW JERSEY DISTRICT					
Chemical analysis	Rockingham clay	Plastic clay (No. 32)	No. 1 fine clay	Plastic clay (No. 38)	No. 2 fine clay	Plastic clay (No. 30)
Ignition loss	9.04	7.54	14.32	5.60	12.38	7.96
Silica	57.20	69.56	43.86	76.24	51.04	65.24
Alumina	25.78	20.34	38.81	15.76	32.31	22.34
Iron oxide	2.78	0.54	0.89	0.52	1.29	1.14
Titania	1.32	1.64	1.84	1.68	1.92	1.36
Lime	0.13	0.25	0.34	0.26	0.37	0.20
Magnesia	1.11	.30	.34	.29	.34	.79
Alkalis	2.60	.26	.31	.23	.12	1.71
Total	99.96	100.43	100.71	100.58	99.77	100.74

TABLE (*Continued*)

		NEW JERSEY DISTRICT					
		Rockingham clay	Plastic clay (No. 32)	No. 1 fine clay	Plastic clay (No. 38)	No. 2 fine clay	Plastic clay (No. 30)
Fusion point	Cone	27–28	30–31	Above 33	30	32–33	30
Firing properties							
Water of plasticity		37.1	30.3	38.7	19.1	37.0	37.3
Drying shrinkage		27.0	22.0	24.5	13.1	27.3	33.9
Av. firing shrinkage							
1200°C		30.6	13.6	33.4	.8	23.6	23.8
1240		34.0	15.4	36.2	1.2	26.0	27.9
1280		30.8	17.2	38.1	1.6	28.4	29.5
1320		21.6	18.7	40.8	2.5	31.4	28.8
1360		18.4	19.8	43.3	2.1	34.3	22.7
1400		15.4	21.5	44.9	1.6	35.6	16.1
1440		13.7	25.4	46.1	.4	38.5	7.7
1480		11.0	29.9	46.2	3.3	39.2	3.0
Av. porosity							
1200°C.		7.1	32.5	27.5	32.3	31.1	15.1
1240		.5	29.6	24.0	32.1	28.9	7.4
1280		.2	27.2	19.8	31.4	25.9	1.4
1320		9.5	26.3	13.5	30.8	22.0	3.2
1360		9.7	25.3	8.9	30.6	16.4	9.2
1400		15.1	22.5	2.6	30.6	12.2	14.4
1440		3.4	17.0	8.2	30.0	8.5	17.3
1480		17.7	6.6	7.7	26.6	6.1	23.3

CHEMICAL ANALYSES AND FIRING PROPERTIES OF FIRE CLAYS FROM VARIOUS PRODUCING DISTRICTS

		PENNSYLVANIA DISTRICT					SOUTHERN OHIO DISTRICT
Chemical analysis		Monument flint clay	Cambria County bond clay	Clinton County flint clay	Dean flint clay	Westmoreland Co. plastic clay	Plastic clay
Ignition loss		14.50	12.68	13.82			10.82
Silica		43.48	44.60	42.76	50.61	56.65	53.32
Alumina		39.20	37.35	39.03	45.33	36.33	29.47
Iron oxide		0.74	1.17	0.77	0.77	1.79	2.29
Titania		2.20	2.16	2.72	2.44	2.95	1.52
Lime		0.26	0.30	0.30	0.26	0.35	0.62
Magnesia		.31	.42	.37	.10	.66	.72
Alkalis		.08	1.57	.14	.24	1.23	.63
		100.77	100.25	99.91	99.75	99.96	99.39
Fusion point	Cone	32–33	32–33	32–33	33–34	30–31	28–29
Firing properties							
Water of plasticity		18.8	16.8	14.2	17.4	19.4	21.3
Drying shrinkage		11.3	10.3	2.9	9.1	19.5	18.0

Av. firing shrinkage						
1200°C	15.6	16.4	15.7	6.0	15.2	16.9
1240	17.9	17.6	16.9	6.2	18.3	18.6
1280	18.0	18.7	15.8	6.6	16.3	19.9
1320	19.1	19.1	14.3	7.4	15.0	19.8
1360	19.3	19.1	11.8	7.2	14.1	19.5
1400	18.4	18.9	13.0	7.1	13.0	19.0
1440	17.6	19.3	9.8	7.0	7.0	14.7
1480	17.4	20.9	10.4	6.7	2.3	7.0
Av. porosity						
1200C°	28.5	23.1	28.3	27.0	18.3	17.2
1240	27.7	22.3	27.3	26.8	12.0	13.6
1280	27.1	20.5	27.8	26.3	7.4	11.1
1320	25.0	20.3	28.1	26.0	4.3	9.5
1360	25.7	19.8	28.4	25.3	3.7	7.1
1400	25.6	19.1	27.6	24.2	2.6	3.6
1440	24.6	17.6	28.2	23.6	3.4	.2
1480	23.8	15.5	26.9	24.3	6.3	11.7

MELLON INSTITUTE
PITTSBURGH, PA.

SEGREGATION IN BINS[1]

By T. W. Garve

ABSTRACT

The formation of a cone in filling a bin causes ground materials to segregate. We have shown that bins will empty first through the center where the fine material is located and that the sides, where the coarser particles are, will follow through the center afterwards. This takes place regardless of the shape or the angle of the hopper bottom within practical limits. A retarder in center will somewhat correct segregation. To overcome segregation fully, the aforementioned cone formation must be avoided.

Segregation on Delivery into Bin

When grained materials such as ground grog and ground clay, even after screening, are delivered from a chute into a storage bin, a heap or cone always forms on top of the fill, which causes the material to segregate. The coarser and heavier particles, having the greater momentum, will roll down and collect at the bottom of the cone, and the finer and lighter particles will remain toward the center or top of the cone.

If the discharge end of the intake chute is located at or near the center of the bin, the coarser particles will be found along the wall of the bin and the finer particles around the center of the bin. If the discharge chute is placed alongside the inner wall of the bin we are getting only half of the cone, but still segregation.

In the manufacture of certain kinds of refractories, and also terra cotta, it is important that such segregation of grogs be avoided, in order to obtain a product uniform in mechanical strength and shrinkage.

The prevention of cone formation would seem the surest way of preventing segregation. One way of accomplishing this would be to devise a flexible spout, the discharge end of which would always have to be on top of the material and moving around continually, so as to keep the top of the bin practically level while the bin is being filled. It can readily be seen that such a device would be complicated.

Another way of preventing cone formation would be to use a continually rotating leveling device with prongs or scrapers to level down the beginning of a cone before segregation sets in. There might be possibilities along this line, although we do not know of any such device.

Segregation on Withdrawal from Bin

Now what is the result in emptying a bin? An interesting article was published in the *Tonindustrie Zeitung* of July, 1915, by Wittich, where it was demonstrated by photographs obtained from a bin model with a glass plate in front and subsequent layers of black and white sand behind, that the material above the bottom outlet would come through first, and that the sides would follow from the top down after the angle of slide is obtained. Figure 1 is a reproduction of one of those illustrations, the second in that series. The author was particularly interested to show that materials poured into the bin last did not come out last, as was generally supposed, but followed through the center instead.

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb., 1925. (Heavy Clay Products Division.)

Influence of Angle at Bottom

We wish to call attention to the dished bin walls used in the experiment. The question is whether or not this same would be true for ordinary bins such as we are using, with a straight hopper bottom, and whether or not this angle of hopper bottom will influence in some degree the manner in which the bin is emptying—especially for larger angles.

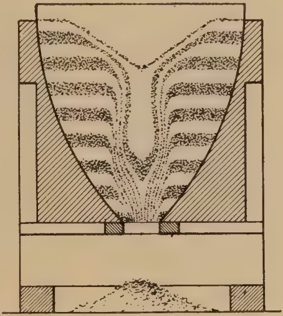

FIG. 1.

It was claimed that the bottom should have an angle of 52° to get material from all over the bin. It was of vital importance for us to know this before large storage bins were constructed.

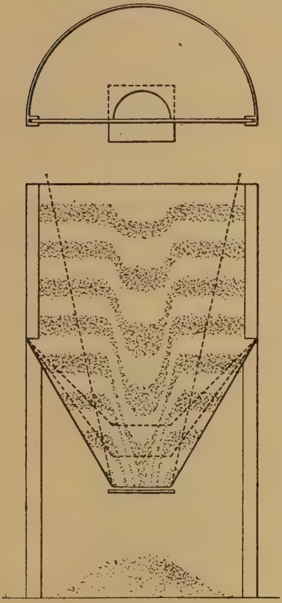

FIG. 2.

We constructed models of semi-circular cross-section, with a glass plate in front. We made hopper bottoms of 45°, 60°, and $52^{1}/_{2}$°. In Fig. 2 we have a drawing of such a bin, the 60° bottom being heavily shaded and the other two hoppers shown in dots and dashes. The bottom slide has been opened a short time and closed again, as the different layers indicate.

In Figs. 3, 4 and 5 we have photos of the bins with the three different hoppers. In Fig. 5 the top layers have followed the downward trend simply because the bottom slide has been kept open a longer period of time. In Fig. 6 the slide was opened still more, until the top layer of white sand formed its natural angle of slide. All the layers resting upon the hopper are still in place, although the tendency later of the center path is to widen out gradually, the adjacent particles being pulled down by friction. The bottom opening is one-fourth of the width of the bin (corresponding to a two-foot feeder cylinder and an eight-foot diameter bin), and this is about all that is coming down at the

FIG. 3.

beginning, while the path will later increase to about one-third of the width of the bin.

A hopper bottom of 60° would be about the limit for a practical bin if storage capacity is not to be jeopardized. However, to make the experiment complete, we constructed a bin with side walls of 77° angle, shown in Fig. 7. At the beginning it emptied like the other bins through its center, but the sides soon began to slip out into the center path, and there was no angle of slide noticeable at any time on top of the fill. It would seem that in such a bin any tendency of the material to hang or bridge would be increased, due to the tendency of the sides to crowd in on the center. All the other hoppers carry the sides.

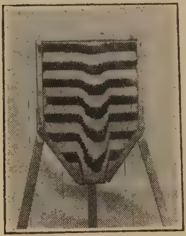
FIG. 4.

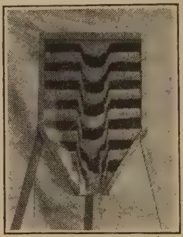
FIG. 5.

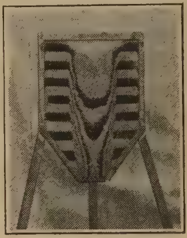
FIG. 6.

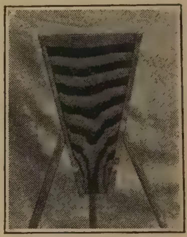
FIG. 7.

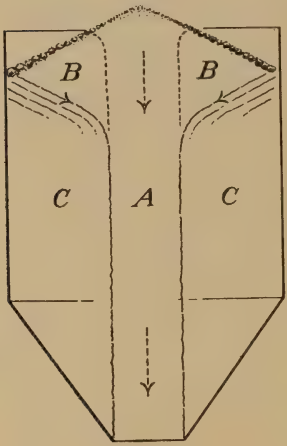

FIG. 8.

The experiment on the first three practical bins shows conclusively that the angle of the hopper bottom would not correct segregation. After the bin above the hopper is completely emptied the slope of the bottom should be steep enough so that the rest of the material will slide out. If this is not desired, a flat bottom is just as good as a cone.

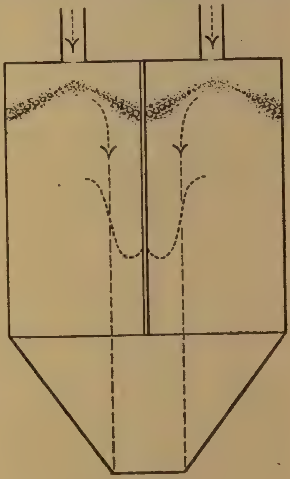
FIG. 9.

Figure 8 summarizes the information obtained. The contour on top of the fill shows the state of segregation as it is to be found all through the bin. The center, *A*, will come down first, then the remainder of the top cone, marked *B*, and finally the sides, *C*, will slide from the top down. In other words, we are getting the finer material first and later the coarser material.

Use of Partitions

It has been suggested to put partitions inside of the bin—in other words, to divide the bin up into smaller sections and to fill each section separately, but to draw from all sections at the same time. This is being done at the Lincoln plant of Gladding, McBean & Co. There is no question but that such bin construction will lessen segregation with reference to the filling of the bin. It had no effect on the method of emptying, as we have demonstrated by experiment.

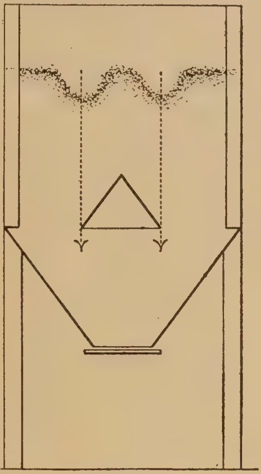

Fig. 10.

In Fig. 9 we have center partitions, one each way, but only one visible in the drawing. We are getting material from four cones, first the coarser particles, but later a mixture of fine and coarse material. Since in such smaller units the cones are lower, the segregation is also correspondingly less pronounced.

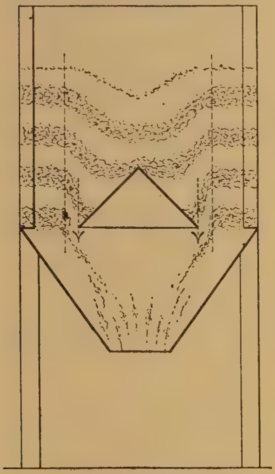

Fig. 11.

The thought suggests itself that a retarder in the center of the bin would help. We used two retarders, one measuring one-third the width of the bin crossways, shown in Fig. 10, and another one measuring one-half the width of the bin, shown in Fig. 11.

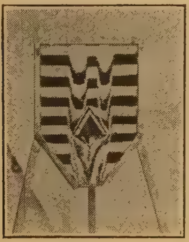

Fig. 12.

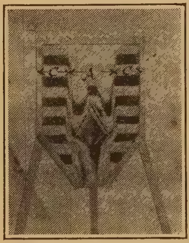

Fig. 13.

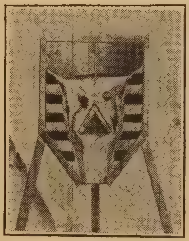

Fig. 14.

This retarding center cone in a round bin will cause the material to come down in a circular depression, taking the material from the center as well as from the sides—hence giving some mixture of fine and coarse material.

With the smaller retarder the apex of the depression was at the outer edge all the way through, as shown by arrows in Fig. 10. In Fig. 11, with the larger retarder, the apex started at the same place, but wedged out gradually as the downgoing material approached the outer edge of the wider retarder. The smaller retarder would be the better of the two, avoiding wedging.

Additional experiments with the smaller retarder are shown in photos, Figs. 12, 13, and 14, in three successive stages of emptying. The retarding cone had an inner flange against the glass plate hence the light outlines above the dark cone represent the actual size. The first material or center path *A* (marked again in Fig. 13) measures, according to the degree of emptiness, from $^1/_2$ to $^2/_3$ of the width of the bin against $^1/_3$ to $^1/_2$ without a retarder. Applying this to a bin of 8-feet diameter would mean that the remaining material on each side, to come out last, measures about 2 feet on each side with a retarder and 3 feet without such. Hence, with the retarder we are getting coarser material at the beginning during the down-path of the center, one foot more on the radius all around.

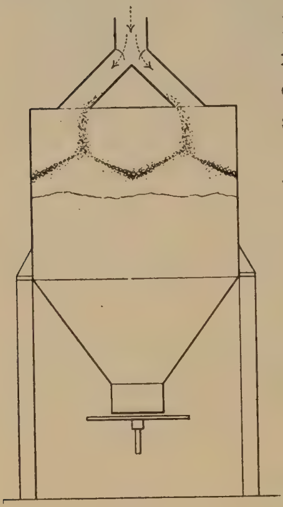
FIG. 15.

The character of the material in question will mainly determine the width of any such retarder. It can easily be placed in any bin. A screen analysis should be made to determine fully whether better results (and how much better) can be obtained. The cost of any such trial is negligible.

Apron to Prevent Segregation on Filling

In Fig. 15 we have one suggestion to better filling conditions by introducing a flaring apron above the bin to divert the material from the center to a ring half-way between the center and the bin wall. The same result is obtained with partitions, as shown in Fig. 9.

As outlined in the beginning, any real remedy must concern itself with avoiding cone formation in the filling of the bin. In one plant segregation was avoided by storing crushed grog, instead of ground grog, which introduces other problems.

GLADDING, MCBEAN & CO.
GLENDALE, CALIF.

THE QUANTITATIVE DETERMINATION OF IRON EXISTING AS FERROSILICON IN ARTIFICIAL CORUNDUM

By R. A. Heindl

ABSTRACT

A procedure is given for determining quantitatively the iron existing as ferrosilicon in artificial corundum.

Object

This research work was undertaken to find a rapid method for the determination of ferrosilicon in artificial corundum. Ferrosilicon has a deleterious effect when present in appreciable quantities in corundum used in the manufacture of fired products.

In the production of artificial corundum a careful analysis is made of all materials entering into its manufacture. The mix which enters the furnace is so proportioned as to produce ferrosilicon which is magnetic (approximately 80% iron), thus making it readily removable with magnets.

Material Used Artificial corundum of 10, 24, 30, 90 and 180-mesh size, which had received the manufacturer's full purification treatment, was used for this work.

Problems Undertaken Determinations of:

1. Total iron both as ferrosilicon and as iron oxide which is present in the grain.

2. Percentage of iron obtained by subjecting the grain to an acid treatment.

3. Percentage of ferrosilicon removed by combing the grain with a magnet.

4. Percentage of iron oxide.

(*a*) In original corundum;

(*b*) In corundum from which ferrosilicon had been removed by acid treatment.

5. Percentage of iron present as ferrosilicon.

6. Percentage of titanium oxide: (*a*) In original sample of corundum;

(*b*) In corundum having received the acid treatment for removal of ferrosilicon.

For purposes of description of the various determinations made the results as obtained from the analysis of 180-mesh corundum are given. A complete tabulation of all results obtained through analyses of the various size grains is given on a following page.

Problem 1. Total Iron

A 2-gram sample of corundum was placed in a 30-cc. platinum crucible and a mixture of 20 cc. of concentrated nitric acid and hydrofluoric acid (3:1) added. The crucible was placed on a hot plate and the liquid completely evaporated with care so as to avoid spattering.

To the contents of the crucible were added 15 grams of fused potassium sulphate and the whole heated over a gas flame until complete solution of the solids.

After cooling the mass was placed in a 300-cc. casserole with 200 cc. of distilled water and 20 cc. of concentrated sulphuric acid. As soon as the liquid had boiled sufficiently to clear, any remaining particles were filtered off, dried, fused and brought into solution as before.

The liquids were combined and treated with washed hydrogen sulphide gas for the reduction of the iron present. (Scott's Chemical Analysis.) The solution was brought to the boiling point during the passage of the gas and at the end of about 10 minutes boiling any platinum sulphide present was filtered off.

The filtrate was boiled in an Erlenmeyer flask until all traces of hydrogen sulphide gas had disappeared. The solution was then rapidly cooled and the iron determined by titration with potassium permanganate. Duplicate determinations gave checking results.

180-mesh corundum	
Per cent iron	0.219
Per cent iron oxide	0.313

The figure of 0.219% represents the total iron present whether in the form of iron oxide or ferrosilicon, and the figure 0.313% simply is the conversion of the iron content 0.219 to iron oxide. This figure is given as oxide to simplify calculations and comparisons further on.

It may be stated that the stannous chloride method (Blair's "Analysis of Iron Ores") for reduction of the iron salts, and also the Jones reductor method, in which 3 cc. of a 10% solution of copper sulphate is added (see Treadwell-Hall "Quantitative Analysis") to suppress the effect of the titanium oxide, were used, but it was impossible to obtain check results and the iron content in all cases was too high.

Problem 2. Iron Soluble in Acid

Ferrosilicon, though difficult of solution in most acids can readily be dissolved in a mixture of 3 parts by volume of concentrated nitric acid and 1 part of hydrofluoric acid.

A 2-gram sample of corundum was placed in a platinum dish and 20 cc. of this acid mix added. The dish and contents were placed on a hot plate and the acid carefully evaporated until about 1 cc. remained. To this was added 15 cc. of concentrated sulphuric acid and evaporation continued for about one hour after strong fuming of the sulphuric acid. The treatment was conducted in this manner to prevent the formation of any insoluble nitrates and to permit the complete removal of all nitric acid. It was found that traces of nitrates in solutions of iron destroy the effect of potassium permanganate to quite an appreciable extent causing consequent high and erroneous results.

The dish and contents were then placed in a porcelain casserole and boiled with 150 cc. of distilled water.

After filtering off and thoroughly washing the corundum the filtrate was subjected to the hydrogen sulphide gas to reduce the iron salts present, boiled to expel excess gas, cooled and the percentage of iron determined with potassium permanganate.

The corundum remaining on the filter paper was carefully washed into the platinum dish, dried and subjected to a second acid treatment identically as described above, and any iron extracted determined with potassium permanganate. The results as obtained on 180-mesh corundum are:

1st acid treatment, 0.168% Fe
2nd acid treatment, 0.008% Fe

These figures show that one acid treatment for grain as fine as 180-mesh removes practically all iron which is present as ferrosilicon. There is a possibility that 0.008% actually represents iron oxide which is present and which is explained in another paragraph.

Referring to the table on page 681 it is readily seen that one acid treatment does not remove all the ferrosilicon in the coarser grains. The larger the grain the less removed. This is of course self-explanatory, since the smaller the grain the more surface is exposed to the action of the acid. By crushing the grain to pass a 150-mesh sieve, after one acid treatment, it was fine enough to permit complete solution of any ferrosilicon present.

Problem 3. Iron Removed by Magnet

Ten-gram portions of original corundum, ground to pass 150-mesh sieve, were accurately weighed and placed on glazed paper. A strongly magnetized horseshoe magnet, having the poles fitted with an envelop to permit the complete and rapid removal of the magnetic material, was passed back and forth through the ground corundum until no further particles of ferrosilicon appeared on the magnet. The resultant ferrosilicon was weighed, care being taken not to include any fine particles of corundum. The result obtained using 180-mesh corundum was 0.02% of magnetic ferrosilicon.

Since this figure represents only approximately 80% of iron in combination as ferrosilicon it is readily seen that this method of separating and determining percentage of iron present as ferrosilicon is of no value, since the actual amount present is several times greater as explained under Problem 5, when determined by chemical analysis.

A portion of the crushed grain from which the magnetic material had been removed with the aid of the magnet after being subjected to a fusion with potassium bisulphate showed the presence of magnetic ferrosilicon.

The removal of only a portion of the ferrosilicon is doubtless due to adhering particles of corundum. Such small particles clinging to or being a part of the finely divided ferrosilicon counteract the attractive force of the magnet.

There is also the possibility of the presence of the small percentage of nonmagnetic ferrosilicon which is not removed by this process.

Problem 4. (*a*) Total Fe_2O_3 and (*b*) Fe_2O_3 Not Removed by Acid

(*a*) A 2-gram sample of corundum, ground to pass 150-mesh sieve, was dissolved by fusing with 15 grams of potassium bisulphate. After cooling, the mass was placed in a 300-cc. casserole containing 20 cc. of sulphuric acid and 200 cc. of distilled water and boiled until clear. After filtering and washing of the paper the iron oxide was determined as before by use of the hydrogen sulphide gas and potassium permanganate. The result obtained for 180-mesh grain was 0.216% iron oxide or 0.149% iron.

(*b*) The determination of iron oxide in corundum from which the ferrosilicon had been removed by the acid treatment was made on samples used in Problem 2, *i. e.*, those having received the acid treatment. A 2-gram sample was fused with 15 grams of potassium bisulphate until complete solution. After cooling, dissolving with water and acid, and boiling, the iron oxide was determined in the same way as under (*a*) above. The result for 180-mesh grain was 0.071% iron oxide or 0.050% iron.

Problem 5. Iron as Ferrosilicon

As stated in Problem 1, the total iron present in the 180-mesh corundum analyzed, whether as ferric oxide or ferrosilicon, was 0.219%. Since the sum of the first and second acid treatments is 0.176% iron and the percentage of iron oxide as determined under Problem 4 is 0.149%, this would give a total of 0.325% iron as present in the grain either as ferrosilicon, iron oxide or both.

Since the combined determinations as shown in Problem 1, show the total iron, both as ferrosilicon and as ferric oxide, to be 0.219% it is evident that either the ferric oxide is attacked in the acid treatment or that the ferrosilicon is attacked in all steps.

When subjecting 10 mgs. of iron oxide to the acid treatment it was found that it readily dissolved. This proved that the iron oxide in the corundum was partially attacked, but not complete enough to permit it being taken into consideration in the calculations. As a matter of fact the grain, after having received 2 acid treatments, in the case of 180-mesh size, showed 0.071% ferric oxide when dissolved in a fusion of potassium bisulphate in comparison with 0.216% (Problem 4-*a*) given in the untreated grain.

Ten grams of finely divided ferrosilicon were subjected to a potassium bisulphate fusion. It was found that even with this large amount of ferrosilicon as compared with the amount actually present in finished corundum grain the action of the fusion was very slight, not over $2^1/_2$ to 3 parts being dissolved out of 100. With the small amount of ferrosilicon actually present in finished corundum this slight action due to the potassium bisulphate fusion is negligible.

When we now review these figures we can definitely establish a value for the ferrosilicon which is present in 180-mesh corundum as follows:

	Per cent iron
Combined acid and fusion treatment	0.219
Fusion of original grain with potassium bisulphate	.149
Iron present as ferrosilicon	0.070

When the silicon-iron ratio of the ferrosilicon is known (in this case approximately 80% is iron) the percentage of ferrosilicon can be easily computed from this final value, which in this case is .070%.

In analyzing the grain for ferric oxide from which all magnetic ferrosilicon possible had been removed with a magnet, it was found that the result obtained was slightly lower than that shown above although within checking results. For all ordinary purposes it should not be necessary to remove the magnetic ferrosilicon before determining the ferric oxide.

Problem 6. Titanium Oxide

For the determination of titanium oxide[1] the solution obtained from the fusion of potassium bisulphate was brought up to 250 cc. in a quantitative flask. Twenty-five cc. of this solution was used for the determination of titanium oxide by placing it in a color tube and bringing it up to 100 cc. with water containing 5 cc. of a 10% solution of hydrogen peroxide which acts as oxidizing agent. The color was compared in the usual manner with a second color tube having a blank made up of water, 5 cc. of hydrogen peroxide and a few cubic centimeters of sulphuric acid. Standardized titanium oxide was added to the blank until the color compared favorably with the unknown. The following results were obtained in the analysis of 180-mesh corundum.

Titanium oxide in sample having received the acid treatment for removal of ferrosilicon—1.55%.

Titanium oxide in corundum having received no acid treatment—3.25%.

These determinations are given as further evidence that the acid treatment attacks other impurities in the corundum besides the ferrosilicon for which it is primarily intended and also gives an approximation of the extent to which the ferric oxide is removed. It is on account of the presence of this titanium oxide that the selective reducing agent is used for determining compounds of iron.

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[1] This procedure is taken from Scott's "Standard Methods of Chemical Analysis."

Conclusions

From the foregoing it may be seen that the iron as ferrosilicon can be determined by the following steps:

1. Determine the total iron whether present as ferrosilicon or ferric oxide by the combined acid treatment and potassium bisulphate fusion.
2. Determine the amount of ferric oxide present by the fusion method with potassium bisulphate.
3. Subtract the iron oxide as determined in the second step from the iron determined in the first step, both figures being reduced to "iron" and the difference represents the percentage of iron present in the corundum as ferrosilicon.

The following table gives the percentages of the iron present as ferrosilicon in the grains on which experimental work was done:

Corundum	Per cent
10-mesh	0.171
24-mesh	.120
30-mesh	.120
90-mesh	.087
180-mesh	.070

The results from analyses of various sized grains follow.

Mesh	10 %	24 %	30 %	90 %	180 %
Total Fe either as FeSi or Fe_2O_3	0.320	0.269	0.269	0.236	0.219
Fe obtained first (*a*) acid treatment	.118	.118	.101	.151	.168
Fe obtained second acid treatment. (*a*) crushed to pass 150 mesh	.117	.101	.084	.050	.008
Fe_2O_3 on above sample after two acid treatments	.115	.071	.090	.06	.071
Fe_2O_3 original sample reduced to Fe	.149	.149	.149	.149	.149
Ferrosilicon removed by magnet	.12	.09	.02	.01	.02
Titanium oxide in original sample	3.30	2.80	2.90	2.85	3.05
Titanium oxide in sample having received acid treatment	1.66	1.65	1.45	1.65	1.55

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ORIGINAL PAPERS

SOME OBSERVATIONS ON THE DRYING PROPERTIES OF CLAYS[1]

BY D. C. LINDSAY AND W. H. WADLEIGH

ABSTRACT

This is a preliminary report. After calling attention to some phenomena brought out, the authors discuss the effects of shape, temperature, vapor pressure, humidity and the velocity of air currents as affecting the rate of drying. It is shown that evaporation from the clay sample is directly proportional to surface area exposed per unit weight of the dry clay body and that successful drying is a function of the rate of drying, but a different function for each different type of clay. Data are presented on the relation of transverse breaking strength to residual moisture content for each of several typical clays. The causes of the varying types of drying injuries are pointed out, sample drying schedules are given and a method is suggested whereby the clayworker may without great expense quickly work out for himself in the laboratory the most rapid and safe drying schedules possible for his particular type of material regardless of its character or its source, and to alter his drying practice so as to overcome present difficulties. Brief descriptions are given of the drying cabinet used and of a simple weighing device for automatically indicating, through loss of weight, the amount of moisture already evaporated and the amount of shrinkage the clay has undergone at any moment of observation during the drying process. The information supplied should operate to bring about a reduction in production costs of clay products, and hence of selling prices, to the ultimate consumer. A brief outline of the proposed extension of the investigation is given in the conclusion.

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[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

I. Introduction

Among the most complex problems encountered by the clayworker is the efficient and successful drying of his ware. No problem of the ceramist has been more neglected, due in part to the large number of factors involved and the complexity of the problem, and in part to succeeding moderately well in the use of natural or uncontrolled means of drying.

The investigation is divided broadly into two parts: first, the determination in the laboratory of the factors controlling drying and the effect of drying treatment upon the physical properties of clay bodies; second, a determination of the drying properties of typical clays from each of the principal deposits of the country.

II. States of Water in Clay

We have used the classification practically as given in the *1921–22 Year Book of the American Ceramic Society*.

1. Water of Plasticity "Water of plasticity" of a clay is all water which can be driven out of the clay in an atmosphere of 4% relative humidity at 110°C.

2. Shrinkage Water "Shrinkage water" is that portion of the water of plasticity which already has been driven off when shrinkage practically ceases.

3. Pore Water "Pore water" is that portion of the water of plasticity still clinging to the surfaces of the grains of the clay substance after shrinkage has practically ceased, but driven out at 110°C in an atmosphere of 4% relative humidity.

4. Hygroscopic Water "Hygroscopic water" is water which remains in the clay after the pore water has been driven off. Thoroughly dried clay will reabsorb a certain amount of water from the atmosphere.

III. Theory of Moisture Removal

The theory of evaporation has been well covered by a number of authors, notably W. K. Lewis[1] and W. H. Carrier.[2] The rate of evaporation of moisture from materials depends upon the following factors:

1. The vapor pressure of the moisture in the material
2. The vapor pressure of the moisture in the air
3. The velocity of the air over the surface of the material
4. The physical properties of the material being dried

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[1] W. K. Lewis, "Rate of Evaporation from Solid Materials," *Jour. Ind. Eng. Chem.*, **13,** 429 (1921).

[2] W. H. Carrier, "Theory of Atmospheric Evaporation," *Jour. Ind. Eng. Chem.*, **13,** 423 (1921).

IV. Factors in Rate of Evaporation from Clays

1. Temperature and Vapor Pressure

The temperature of a drying clay body,[1] does not reach the temperature of the surrounding air until it ceases to lose moisture, and this occurs only when the vapor pressure of the clay moisture is equal to that of the air moisture. Figures 1 and 2 show graphically the temperatures observed within two clay bodies during drying, and also the dry and wet bulb temperatures of the surrounding air. The mean rate of moisture loss the first eight hours from the clay of Fig. 1 was slightly greater than for clay of Fig. 2, due possibly to the average relative humidity of the air being slightly lower in the case of the clay of Fig. 1 than it was in that of Fig. 2. However, the observations recorded in Fig. 1 apply to a coarse 50% grog body, while those of Fig. 2 apply to a dense English ball clay. Knowing the wide difference in the porous structure of these two bodies, a difference in drying rates might have been expected even if the relative humidities of the respective surrounding atmospheres were the same.

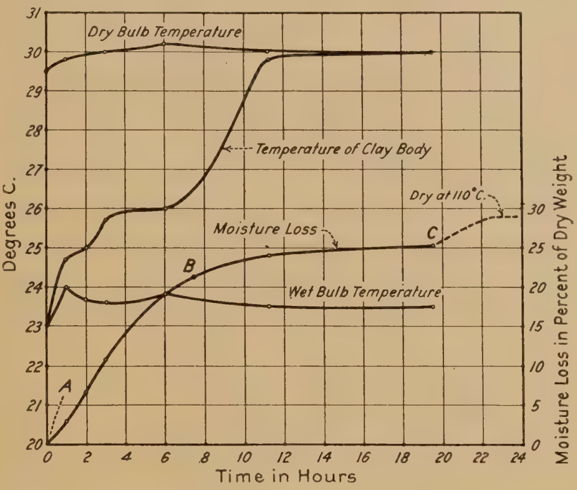

Fig. 1.—Internal temperature of clay during drying. Sagger clay. 50% grog.

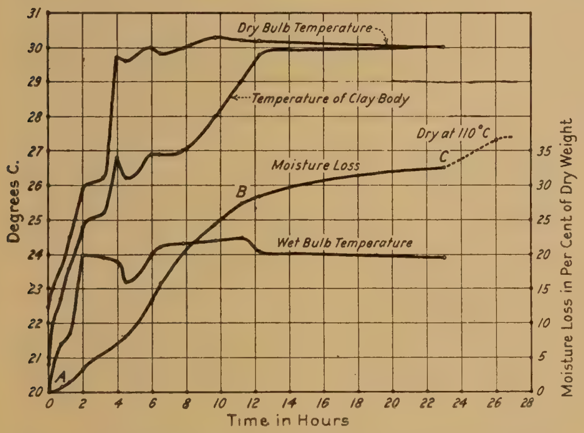

Fig. 2.—Internal temperature of clay during drying. English ball clay. B–5.

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[1] In this investigation the temperature was determined by inserting into the plastic clay body the bulb of an ordinary mercury glass thermometer.

Figures 1 and 2 show, not the actual moisture loss in grams but the observed loss of moisture, in per cent of the dry weight of clay, corresponding to the time of drying. These curves of Fig. 1 after the first four hours and of Fig. 2 are typical of the drying of clays under conditions of constant temperature and humidity of the surrounding air. For convenience in discussion the moisture loss curves may each be divided arbitrarily into two sections: *A–B* and *B–C*.

From *A* to *B* the moisture loss proceeds, roughly, at a uniform rate. Beyond *B* during the stage *B–C* the rate of evaporation decreases continuously, approaching a state where no further moisture loss occurs at that temperature and humidity. Simultaneously with this decrease in rate of evaporation the temperature of the material rises, rapidly approaching the dry bulb temperature of the air.

The rate of evaporation during the time *A–B* is approximately described by the equation for evaporation from a free liquid surface:

$$dw/dt = (e' - e)C$$

where dw/dt = rate of evaporation
e' = vapor pressure in the material
e = vapor pressure in the air
C = a constant for a particular clay

The principal cause of deviation from this rate equation seems to be shrinkage; the progressive reduction of evaporating surface together with the decreasing moisture content is doubtless responsible for the slow decrease in the rate of evaporation shown near point *B*.

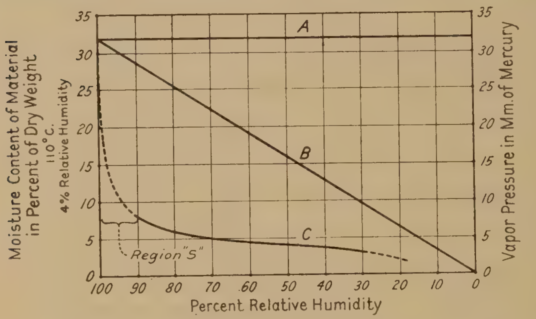

FIG. 3.—Theoretical *vs.* actual vapor pressure in clay. Constant temperature of material = 30°C. Key: *A*—Vapor pressure maximum at 30°C. (Clay saturated.) *B*—Vapor pressure in material corresponding to moisture content. *C*—Normal moisture content of material corresponding to relative humidity.

The rate of evaporation during the time from *B* to *C* does not follow the laws applying to time *A–B*, and is complicated by numerous factors. The vapor pressure of the water still remaining within the material does not even approximate the vapor pressure of free water at the temperature of the material. The water remaining is not free water, but adheres to the walls of the pores and capillaries. Its vapor pressure is reduced probably by capillary restriction, by a natural affinity between the water and the material, and possibly by a colloidal relation with which we are not familiar.

This reduction in vapor pressure below that corresponding to the temperature of the material is well illustrated in Fig. 3. It is a familiar fact that any hygroscopic material placed in an atmosphere of fixed humidity will come to an equilibrium weight in that atmosphere, gaining or losing moisture according as its initial vapor pressure is less or greater than that of the atmosphere. Curve *C*, Fig. 3, represents the recorded equilibrium conditions for a clay[1] during the process of drying at various humidities and a constant air temperature. Line *A*, Fig. 3, is the maximum vapor pressure which could exist in the clay at the constant temperature of 30°C. Line *B*, Fig. 3, indicates the vapor pressure in the air and also the actual vapor pressure in the clay at the various relative humidities, since to be in equilibrium the effective vapor pressure of the evaporating liquid in the clay must be equal to the vapor pressure in the atmosphere. We may note also that in this figure the vertical distance between lines *A* and *B*, for any given humidity, represents the difference between the pressure of saturated water vapor, corresponding to the temperature of the clay, and that vapor pressure which actually exists in the clay.

These observations of equilibrium conditions were made in a drier in which it was not possible to maintain a satisfactorily constant relative humidity above 90%, so that between 90% and 100% relative humidity, curve *C* is simply approximated. We know, however, that at 100% relative humidity there would be no evaporation from the clay and that the moisture equilibrium points between 90% and 100% must lie along some such extension of the curve as shown in Fig. 3 and designated "region *S*." We observe also from Figs. 1 and 2 that down to a residual moisture content of about 8% of the dry clay weight evaporation proceeds at a nearly uniform rate, which means that the moisture is evaporating essentially as from a free liquid, and therefore, that its vapor pressure is the same, or only slightly lower, than that corresponding to the temperature of the clay. In order to satisfy this condition, the ordinate of curve *C*, Fig. 3, must have an initial value equal to that of the maximum vapor pressure line.

2. Velocity of Air over Material

The air serves: first, as a conveyor of heat to the clay body; second, to sweep away the saturated vapor from the drying surface. Up to a certain critical velocity the rate of evaporation from a free liquid surface maintained at a constant temperature increases in approximately direct proportion to the velocity of the air over the surface.[1] For such a free liquid surface this critical velocity is very large, but for a drying clay body it is probably never more than about three meters, or ten feet, per second.

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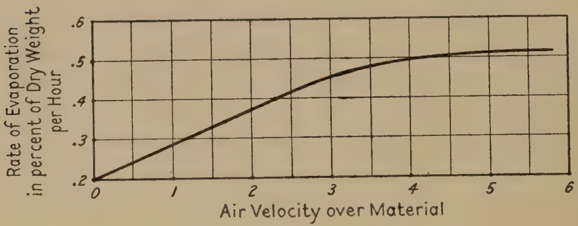
[1] In the case of this particular clay, it so happens that in a saturated atmosphere at 30°C its moisture content expressed as a percentage of dry weight of clay is just equal numerically to the vapor pressure expressed in mm. of mercury, and hence the moisture content and pressure have been plotted to the same scale. At other temperatures or with a different type of clay, it would in general be necessary to plot these to different scales.

On the other hand while as applied to the drying of clays, the law doubtless holds initially, the "critical" air velocity must here be defined as that velocity at which the air current removes moisture from the clay surface at a rate equal to the rate of moisture diffusion from the interior of the wet clay body, and for some clays is probably somewhat less than the above mentioned value. Beyond this critical value any increase in air velocity has little effect upon the rate of evaporation. While no actual velocity measurements have been made during this investigation to determine this limiting rate as applied to clay, Fig. 4, based upon observations of others, indicates the character of the effect.[1]



(Meters per second)

FIG. 4.—Relation of evaporation to air—velocity.

TABLE I

COMPARISON OF DRYING RATES OF SEVERAL CLAYS HAVING DIFFERENT POROSITIES

Specimen 1" x 1" x 7"	Type of clay	Dry bulb temp. of air, °C	Relative humidity, per cent	Rate moist. loss, per cent per hour	Av. poros. per cent, dry volume
K–2	North Carolina kaolin	30	85	0.8	41.5
B–2	English ball clay	29	85	0.3	38.5
B–3	English ball clay (same as B–2)	30	85	0.28	39.5
FE–4	Whiteware body	31	86	0.8	32.7
P–2	Whiteware body	32	86	0.5	30.5

Effective velocity of air over specimens the same in all cases.

3. Physical Properties

Other factors affecting the rate of evaporation from clays are (*a*) internal structure (porosity) and (*b*) form (surface exposed relative to mass).

(*a*) Porosity

It is generally considered that the ease with which a clay may be dried depends upon the porosity of the molded material. Undoubtedly it is true that a *given clay* may be made to dry more rapidly by increasing the porosity through the addition of grog or other coarse material. In comparing the drying rates of *different* clays, however, it has been found that the measured porosity of the dried specimen may not be relied upon solely as a comparative indication of the rate of drying. Table I is a comparison of the drying rates of several clays under practically identical air conditions. Such a comparison would lead one to believe that the rate of evaporation from clays, other conditions being constant, depends more upon the *type* of porous structure, than upon the *amount* of *pore* space.

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[1] W. H. Carrier, Jr., "The Temperature of Evaporation," *Jour. Amer. Soc. Heat. and Vent. Eng.*, **24**, 25 (1918). Also Coffey and Horne, "Theory of Cooling Powers Compared with Results in Practice," *Jour. Amer. Soc. Refrig. Eng.*, **2**, 25, May (1916).

(*b*) **Form** It is a common observation that massive clay pieces dry more slowly than light ware, when exposed to like conditions. As a basis for comparing the drying weights of different masses and forms of the same clay, we have chosen as a term to express this difference—the area exposed per unit mass of clay. For instance, a cubic centimeter of clay which weighs one gram, having dimensions 1 x 1 x 1 cm. and having five faces exposed to the air, has an exposed area of 5 sq. cm. per gram. A like weight of clay, having dimensions 2 x 2 x 0.25 cm., standing on edge, has an exposed area of 9.5 sq. cm. per gram.

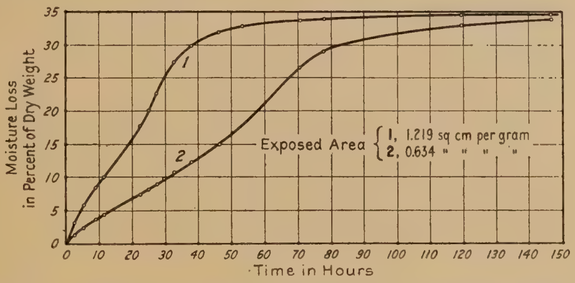

FIG. 5.—Variation in drying rate relative to area exposed per unit mass.

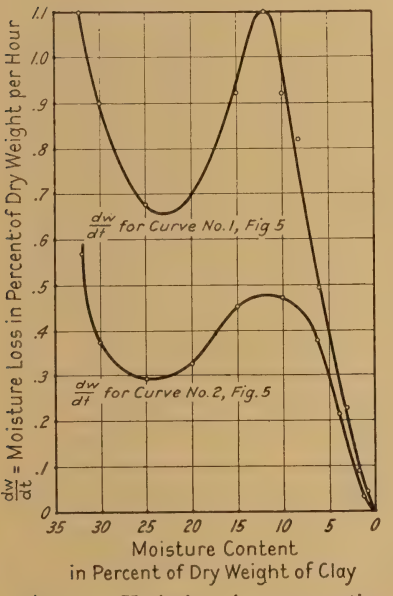

FIG. 6.—Variation in evaporation rate with water content and area per unit mass.

The results of several laboratory tests to determine the effect of variation in surface exposed upon the rate of drying have shown that the instantaneous rate of moisture loss from identical clays, other conditions being constant, varies approximately in direct proportion to the surface exposed per unit dry weight of the clay.

Figure 5 illustrates the results obtained in drying two specimens of English ball clay under identical conditions. Curve 1, Fig. 5, shows the loss of moisture, in per cent of dry weight, plotted against time and is for a specimen approximately cubical in form, having 1.22 sq. cm. per gram of clay exposed to the air. Curve 2, Fig. 5, is the loss curve for a like specimen, which has 0.634 sq. cm. per gram of clay exposed to the air, slightly more than one-half that of No. 1. It will be observed that at all identical stages of moisture loss, Curve 1 rises at about twice the rate of Curve 2. This is shown in Fig. 6 where the instantaneous rates, dw/dt, *i. e.*, the tangents of the curves in Fig. 5 are plotted against the per cent of moisture remaining in the corresponding specimens.

If, now, the rate of evaporation varies directly with area exposed per unit weight, we may state that, other conditions being identical, the rate of evaporation, in per cent of clay weight, varies as the area exposed to the air per unit weight of clay, and is the same regardless of size or shape.[1]

This relation may be expressed as $r_1/a_1 = r_2/a_2$.

Table II gives the values of r/a from data plotted in curves of Fig. 6. Comparison of the rate-area relations shows r/a to be essentially constant. This relation is useful in estimating the drying rates of commercial ware from observations made on laboratory specimens.

TABLE II

COMPARING THE RATE OF EVAPORATION IN PER CENT (RELATIVE TO DRY WEIGHT) Per Hour, per Square Centimeter Area Exposed, per Gram (Dry Weight)

Moisture content of specimen in per cent dry weight (w)	Area exposed, sq. cm. per gm. (a_1)	Area exposed, sq. cm. per gm. (a_2)	Moisture loss, per cent per hour (r_1)	Moisture loss, per cent per hour (r_2)	$\frac{r_1}{a_1}$	$\frac{r_2}{a_2}$
30	1.2193	0.6342	0.66	0.34	0.540	0.537
25	1.2193	.6342	.67	.30	.550	.475
20	1.2193	.6342	.72	.33	.590	.521
15	1.2193	.6342	.97	.47	.795	.740
10	1.2193	.6342	.98	.49	.803	.773
5	1.2193	.6342	.34	.16	.278	.252

4. Summary of Factors Affecting Evaporation

Other factors remaining constant: Rate of evaporation increases with rise in temperature of air, due to increase of effective vapor pressure in the material.

Rate of evaporation decreases with rise in wet bulb temperature of the air, due to the corresponding rise in relative humidity and corresponding reduction in the difference between the vapor pressure in the material and the vapor pressure in the air.

Rate of evaporation decreases, after shrinkage water has been removed, with decrease in moisture content, due to demonstrated decrease in effective vapor pressure in the material. (See Fig. 3.)

Rate of evaporation is increased by increasing the exposed surface area per unit weight of body.

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[1] Of course, in complicated shapes conditions may be introduced which would prevent the body from being exposed to uniform conditions of air over its entire surface.

V. Effect of Rate of Evaporation upon Clay

Having made the foregoing analysis of the factors affecting the rate of evaporation from clays, the effect of rate of evaporation upon clay bodies should be examined.

1. Classification of Clays

Lovejoy has classified clays,[1] with respect to their drying qualities, as follows:

(*a*) Clays that may be dried in a few hours, starting with an initial high temperature and rapid drying conditions.

(*b*) Clays that may be dried in 24 hours or less, starting at an initial low temperature in saturated atmosphere.

(*c*) Clays that can be dried in 24 hours to 72 hours, under conditions of (*b*).

(*d*) Clays that require over 72 hours under conditions of (*b*).

(*e*) Clays that must be slowly heated up in a saturated, stagnant atmosphere before advancing into a moving drying atmosphere.

(*f*) Clays that cannot be safely subjected to conditions under (*b*) or (*e*), but must be dried slowly, starting under drying conditions (*i. e.*, in an unsaturated atmosphere).

(*g*) Clays that cannot be dried under any conditions.

For the purpose of this discussion, we accept this classification, pending the completion of our classification of clays according to their drying properties.

2. Success in Drying Depends upon Rate

In the drying of any clay body, the rate of evaporation from the surface relative to its replacement by diffusion from within, is the all-important factor. According to the foregoing classification, there are clays which may be subjected to an extremely high rate of moisture removal without injury to the mass, while at the other extreme there are clays which can not be dried without cracking or other injury under any circumstances.

3. Types of Drying Injuries

The types of drying injuries of most common occurrence in clay bodies are: warping, breaking, large cracks, checking (fine cracks distributed uniformly over the surface), cracking along laminations, strains.

(*a*) Warping and Cracking

Warping is caused by a non-uniform rate of drying between opposite surfaces of the clay body. It is simply the adjustment of the semi-plastic mass to an uneven rate of shrinkage throughout the body. Warpage has been observed to occur in laboratory briquet specimens under the following conditions: Specimens placed on pine boards and subjected to a highly humid atmosphere, warped up from the board in an arch, leaving two ends in contact. In this case, the board was absorbing water from the under side of the specimen at a greater rate than evaporation occurred from the exposed surfaces; a difference in shrinkage between the two sides was the natural consequence. Again, warpage has been observed to occur in the direction opposite to that just described, when the exposed surfaces are subjected to a current of air which carries the moisture away at a rate greater than the surface replacement by diffusion. Warpage occurs most frequently in light wares. The same causes bring about cracking in heavy ware when the mass of the clay is too great to be shifted or lifted by the strains resulting from uneven shrinkage.

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[1] Ellis Lovejoy, "Drying Clay Wares," T. A. Randall & Co. (1916).

(*b*) **Checking** Checking in ware is caused, not by an uneven rate of moisture removal from the different surfaces of the ware, but by excessive rate of evaporation from the entire surface. When evaporation from the surface occurs at a rate greater than that at which moisture is being replaced by diffusion from within, an excessive rate of surface shrinkage occurs. The result of this is a compression of the inner core of the body. The strength of the shrinking surface layer is not sufficient to withstand this strain and so breaks along rather uniform strain lines, much like crazing in glazes. These cracks, fine at first, often penetrate far into the body before drying is completed.

(*c*) **Laminations** Laminations in a ware are a common cause of drying cracks. The probable initial cause of laminations rests in defective molding of the ware, and is often first seen in the dried, or unfired, piece. A lamination occurs as a fold or dividing space within the body of the clay. Transfer of moisture across the interrupted channels of such a space is difficult. Water tends to collect in this space, there to build up later a vapor pressure with the rise of drying temperature. Most often it happens that such a pressure forces the water out along the lamination plane and, in so doing, ruptures the ware.

(*d*) **Strains** Strain in dried clay ware is a less tangible term than any of the other defects mentioned. We are not sure that strain exists in dried ware that is apparently uninjured. We can only judge by the comparative dry strength of pieces alike as to porosity and other properties, and by those pieces which fail in the early firing stages. It is certain that dry clay has little elasticity and that strains of any considerable magnitude, set up during the drying process, must result in warping or cracking. Cracking that has thus occurred may be made up of very minute lines, not readily detected by the eye, but which appreciably reduce the strength and cause almost certain failure in the kiln.

(*e*) **Sticking** An additional injury frequently found is the tendency of the wet specimen to stick to the drying pallet. As shrinkage proceeds, if the body does not readily slide on the pallet, the resulting strain causes the body to crack across the contact surface.

VI. Drying Schedules and Physical Properties of Clays

1. Selection of Clays for Test

A portion of this investigation has been to select clays for which various safe drying schedules were to be found and the physical properties of the specimens dried under different conditions compared. The selection of clays for this part of the investigation was made for the purpose of finding what physical properties are affected in drying, rather than for a study of the particular clay. The clays thus far treated have been:

(*a*) Specimens composed entirely of English ball clay
(*b*) Specimens composed entirely of North Carolina kaolin
(*c*) Several whiteware body compositions
(*d*) Several clays used in the manufacture of common brick
(*e*) Several shales

2. Maximum Rate vs. Efficiency

The first problem in drying is to find a safe drying schedule. In plant practice, other factors may enter in the most effective rate of drying. The maximum safe rate of drying is not necessarily the rate of maximum efficiency, due to the additional total heat required to evaporate water at increasingly high temperatures.

Figure 7 is an example of a safe schedule found for a semi-porcelain body made into standard briquets (1″ x 1″ x 7″). Conditions of temperature, relative humidity and air velocity were controlled and observed throughout the process. The graphical record of moisture loss and air conditions often shows where the drying may be safely hastened and how the schedule might be shortened, as is well illustrated in Fig. 7.

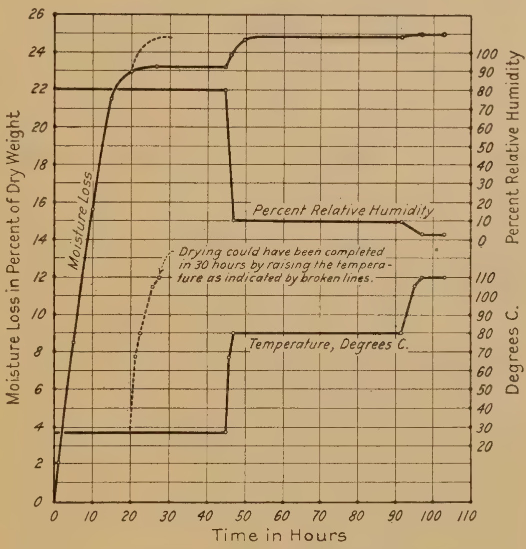

FIG. 7.—Example of drying schedule for semi-porcelain body. P–3–0.

3. Observations and Factors in Establishing Drying Schedules

Figure 8 is a schedule similar to Fig. 7, except that it is the drying record of an extremely plastic clay body, having a large shrinkage factor. In this case, the progressive linear shrinkage was observed simultaneously with the weight loss.

The observation of the rate of shrinkage and the point at which shrinkage is completed, is extremely important in establishing drying schedules. It will be observed that, in the first stages of drying, shrinkage progresses by an approximately uniform rate along a curve similar in form to the Moisture Loss Curve. At a definite point the rate of shrinkage decreases abruptly and approaches a condition where shrinkage is completed. Up to, and especially immediately preceding, this point where shrinkage ceases the clay body being dried is in a critical state and can easily be injured by an excessive rate of moisture removal. Beyond the point where shrinkage is practically completed, drying may be safely hastened to the end by increasing, in proper steps, the temperature and velocity of the air and by reducing the humidity.

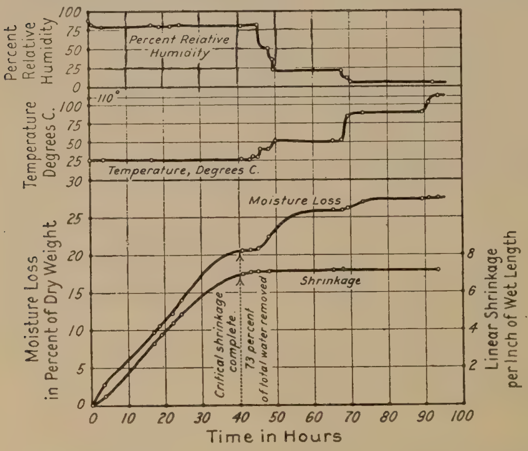

FIG. 8.—Example of drying and shrinkage schedule plastic clay. M–1.

4. Strength of Specimens Dried at Different Rates

Although we have some evidence that the strength of apparently uninjured dry ware is affected by the rate at which drying has taken place at the various stages, we are not yet prepared to present conclusive data. The modulus of rupture of raw clay specimens, molded with extreme care in the attempt to obtain uniformity of structure, at the best varies over a rather wide range between like specimens. If dry porosity be taken as an index of structure, the variation in strength does not seem to be entirely justified by the slight variation in porosity.

TABLE III

COMPARISON OF THE MODULUS OF RUPTURE WITH POROSITY

English ball clay B-3-W specimen no.	Modulus of rupture, lbs. per sq. in.	Porosity in per cent of dry volume
1	417	40.22
2	314	41.10
3	399	40.69
4	361	41.00
5	346	41.99
6	428	40.39

Table III shows the strength and corresponding porosity of a set of English ball clay specimens dried under identical conditions.

5. Variation in Dry Strength According to Residual Moisture Content

The strength of dried specimens, we found, has a decided and consistent variation according to the residual moisture of the specimens. The curves presented in Figs. 9, 10 and 11 show this variation for three different bodies. The curve in Fig. 9 is for a standard semi-porcelain body; Fig. 10 is for a plastic Texas clay used in common brick, and Fig. 11 represents an Iowa shale. The amount of moisture remaining in the body is stated in per cent of weight of the body when dried to a constant weight in air at 110°C and about 4% relative humidity.

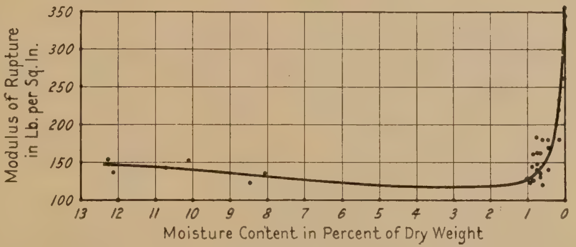

FIG. 9.—Relation between moisture content and modulus of rupture. Semi-porcelain body. P-3-0.

These samples were broken, then immediately weighed and weighed again when dried under the above conditions, in order to find the per cent moisture remaining at the time of breaking. The curves pass through the mean of the moduli observed. The decided increase in strength, with the removal of the last per cent of water, is notable in each case, particularly that of the semi-porcelain body.

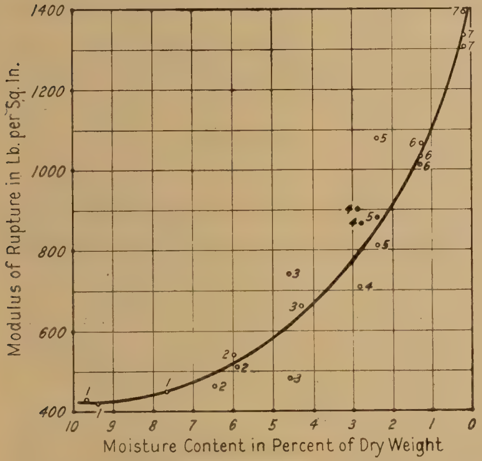

FIG. 10.—Relation between moisture content and modulus of rupture. High plastic clay. M-2.

The moisture regain of these three bodies, during several weeks at average room temperature and humidity, was found to be:

Semi-porcelain body.......	0.7%
Shale....................	0.7%
Texas clay................	2.5%

A decrease in strength corresponding to moisture regain, occurred in shale and clay.[1]

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[1] We found a marked increase in strength with aging in the dry state in English ball clay specimens, some semi-porcelain bodies and North Carolina kaolin specimens. This seems to be independent of the change in moisture content. We are not prepared to make a definite report upon this peculiarity.

VII. Conclusion

This is intended to be only a preliminary report of the drying investigation to date. We have emphasized the factors which govern drying and pointed out the injuries that may occur to clay products when these factors are disregarded.

We believe safe drying schedules used in practice may be approximated in the laboratory from samples of the body and a description of the ware manufactured. By the same laboratory methods and a history of the treatment to which the ware has been subjected it is possible, in most cases, to locate the cause of drying injuries.

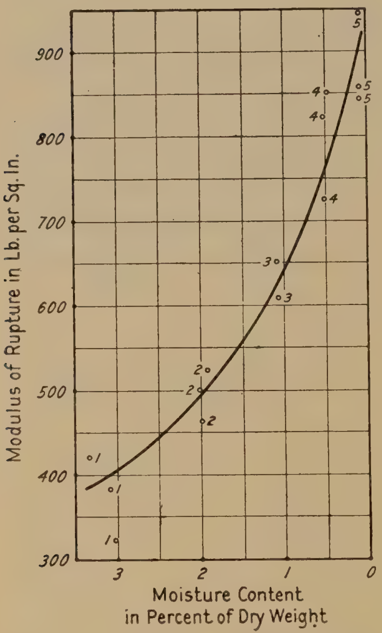


FIG. 11.—Relation between moisture content and modulus of rupture. Iowa shale. A–1.

This survey will be of use in selecting drying equipment, and in altering drying practice to overcome present difficulties.

The methods of controlling drying conditions in the plant are a part of the investigation as yet untouched. Perhaps this portion of the work should rest with the manufacturers themselves and with concerns engaged in the design and manufacture of driers. There are already several forms of equipment admirably suited to cope with plant drying problems.

Appendix.

Processing Cabinet For the purpose of controlling temperature, humidity and air circulation in drying, a Carrier Ejector Processing Cabinet was used. This has proven to be a convenient and useful piece of laboratory equipment. Figure 12 is a longitudinal cross-section of the cabinet showing the arrangement of specimens and indicating the air circulation.

Humidity Control The relative humidity within the cabinet is controlled by means of an adjustable hygrostat mounted on the outer casing and having, protruding into the cabinet, a silk member sensitive to variations in relative humidity. The hygrostat acts upon an atomizing water spray nozzle located near the fan's intake. The instrument will maintain the relative humidity within 3% of the value for which it is set.

Temperature Control The heating of the air is done by electrical elements located at the fan intake. Temperature is controlled by means of a thermostat adjustable from the exterior of the cabinet. The thermostat operates within an accuracy of about 1°C above or below the mean.

Velocity The velocity of the air over the material may be adjusted as desired by the use of a damper in the air supply duct or by varying the speed of the fan motor.

Moisture Loss and Shrinkage Observations By means of a balance, located on top of the cabinet, and the specimen pan suspended by an extension link within the cabinet (see Fig. 12), frequent observations of the moisture loss can be made, without interruption of the drying conditions. It was from such observations that the above mentioned moisture loss curves were plotted.

Shown also in Fig. 12 is a continuous shrinkage micrometer devised for this work. This is comprised of two horizontally adjustable heads mounted upon a slotted bedplate. Upon each head is mounted an Ames dial micrometer (1/100 mm. div.). The specimen is placed upon a pallet as shown and observations of shrinkage made simultaneously with the observations of weight loss from a like specimen upon the balance pan. Such comparative observations of moisture loss and shrinkage are important, as previously pointed out.

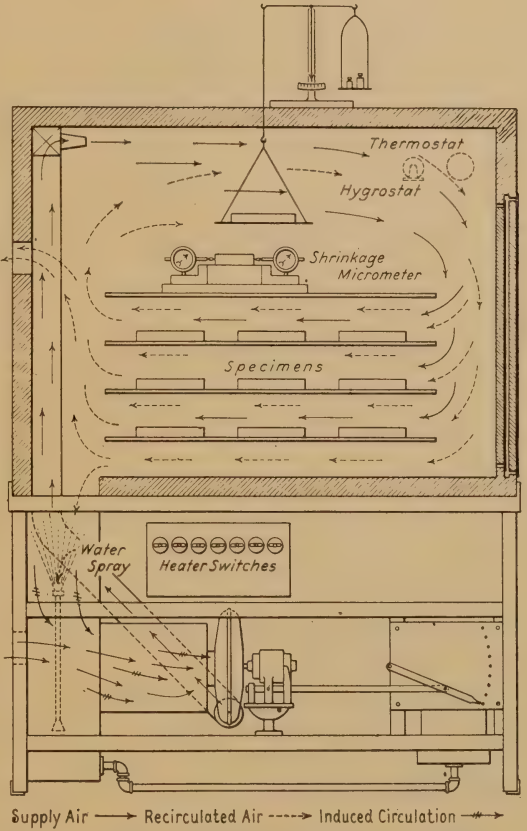
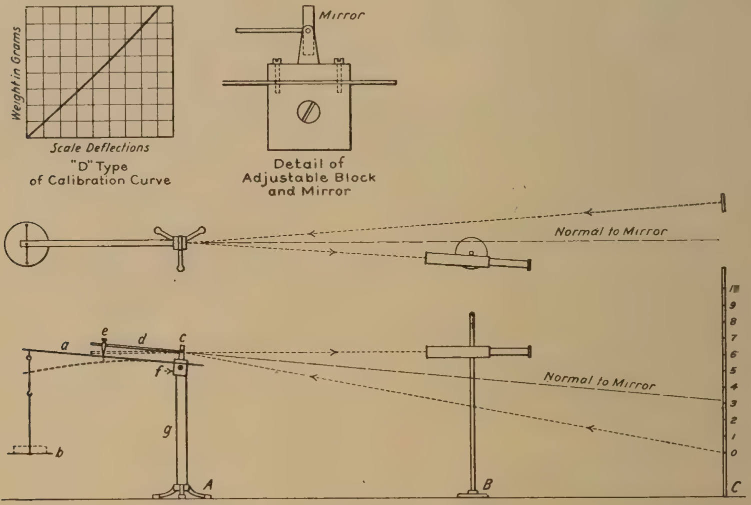


FIG. 12.—The Carrier Ejector Processing Cabinet.

Optical Flexure Balance One of the most tedious tasks in studying the physical properties of clays is the numerous weighing operations, particularly in the determination of porosity. This work was greatly facilitated by the development and use of an optical flexure balance as hereinafter described.

Figure 13 is a diagram of the apparatus used. The principle is simply that of the optical lever in which small deflections of a flexible steel member are magnified through the use of a mirror, a distant scale and a telescope. Object *A* is the balance. *a* is the flexible steel strip (a hack saw blade is suitable) clamped in the split block *f*. The length of the flexible strip, and therefore its deflection per unit weight, is adjustable by loosening the clamp and sliding it backward or forward. *b*, the specimen pan, is suspended by links as shown. *c* is a small mirror pivoted on either side on top of block *f*, and capable of turning as the arm is deflected. Rod *d*, attached to the back of the mirror *c*, rests upon the flexible arm through the adjustable knife edge *e*. *B* is an ordinary laboratory telescope. *C* is a scale adjusted on an angle, as shown, and at a distance governed by the focal length of the telescope and by the desirable amount of deflection magnification.



"D" Type
of Calibration Curve

Detail of
Adjustable Block
and Mirror

FIG. 13.—Optical flexure balance.

The following members of balance *A* are adjustable for calibration purposes: Flexible arm *a*, adjustable as to length; knife edge *e*, adjustable along rod *d*, to vary deflection of mirror *c*; block *f*, adjustable about an axis perpendicular to pedestal *g*, to adjust zero deflection from scale.

Calibration Calibration is accomplished by placing successive known weights upon the pan and plotting a curve—weight *vs.* scale deflection. The curve will not be a straight line following Hooke's Law, but will be slightly concave as shown in *D* (Fig. 13). This is due to the fact that flexible arm *a* and rod *d* turn about different centers.

Sensitivity As used, adjustment was made to cause a deflection of approximately one-half centimeter per gram. The scale used was divided into millimeters. With this scale it was possible to read accurately to $^{1}/_{5}$ gram. Using the cross hair in the telescope $^{1}/_{10}$ gram could be estimated. Numerous checks of weights with a precision balance showed a maximum error of $^{1}/_{10}$ gram. In 50 gram specimens (which are convenient), this amounts to an accuracy within $^{1}/_{5}$ of 1%.

The balance is found to be particularly convenient and useful in weighing materials suspended in oil or other liquids. It is only necessary to suspend the pan in the liquid, note the new zero reading, then proceed in the usual manner to place specimens on the pan as immersed in the liquid.

PROGRESS REPORT ON RESEARCH OF PAVING BRICK FROM IOWA SHALES[1]

By D. A. Moulton

ABSTRACT

Test on full size pavers made from 11 shales showed that five would make an excellent paving material and others had possibilities of making a block that would give service. Various processes were tried as soft-mud, roller expression machine, dry-press, and a new belt machine, also additions of magnesium and colloidal materials. The soft-mud, roller expression machine gave equal if not better results than the stiff-mud process, and the other processes required higher temperatures to get a suitable block for test. Magnesium reduced the rattler test from 27% to 22% and changed the color to a buff similar to that of fire clay. The colloidal materials made the shale more refractory and hence the brick were too soft for the rattler test.[2]

Use	General average loss	Maximum permissible loss
Heavy traffic	22%	24%
Medium traffic	24%	26%
Light traffic	26%	28%

Paving brick have been made for some time in Des Moines, Ia., and there have been attempts to make paving block in other parts of the state. Eleven shales were selected in the various clay-working districts of Iowa.

1. Standard Brick Co., Oskaloosa, Ia.
2. Lehigh Sewer Pipe Co., Lehigh, Ia.
3. Flint Paving Brick Co., Des Moines, Ia.
4. Van Meter Tile Co., Van Meter, Ia.
5. Kalo Brick & Tile Co., Fort Dodge, Ia.
6. Boone Paving Brick & Tile Co., Boone, Ia.
7. Morey Clay Products Co., Ottumwa, Ia.
8. What Cheer Clay Co., What Cheer, Ia.
9. Redfield Brick & Tile Co., Redfield, Ia.
10. Davenport Brick & Tile Co., Davenport, Ia.
11. Adel Clay Products Co., Adel, Ia.

Description of Samples

Samples 1, 7 and 10 are dark colored shales containing organic materials and other carbonaceous materials which require some time to oxidize completely in the firing of a block as thick as paving brick. All fire to a good red color vitrifying in a safe range of temperatures.

Samples 2, 3, 5, 6, 8, 9 and 11 are red to reddish brown with streaks of blue running through the shales in some samples. All are quite free from excess of carbonaceous materials, being easily oxidized and having a good range of vitrification.

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[1] Presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, February, 1925. (Heavy Clay Products Division.)

[2] The American Society for Testing Materials has not given any definite specifications in regard to results required of the rattler test, leaving this to be decided by local conditions. However, they give the following for maximum permissible loss and the general average loss in this test.

Sample 4 is a very soft plastic shale firing to an excellent red color but developed a brittle brick which did not stand the rattler test.

Process of Manufacture The ground shales were pugged both by hand and by wet pan and wedged by use of large wooden mallet, into rectangular pieces 9 x 9 x 24 inches to fit in an iron receiver on a plunger machine which is operated by hand; the crank is connected by gears to the plunger thus increasing the power. This plunger forced the clay out of a die $4^{7}/_{16}$ x $3^{5}/_{16}$ inches into a column of clay which was cut into $8^{3}/_{4}$-inch lengths, thus making an end cut brick. This preparation was designed to make brick of similar structure as is done in commercial plants and was accomplished to a surprising degree as shown by the rattler loss on a brick made in plant and those made of same clay in the laboratory running very close together. There was no

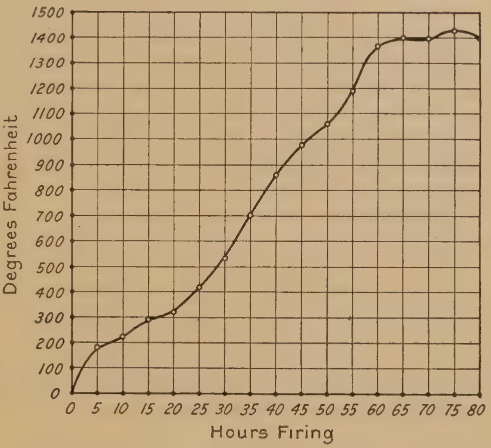

FIG. 1.—No. 1 firing. Paving brick. Cone 04 down. 77 hours to 1480°F. Sample numbers 1, 4, 9, 10. Lower temperature clays.

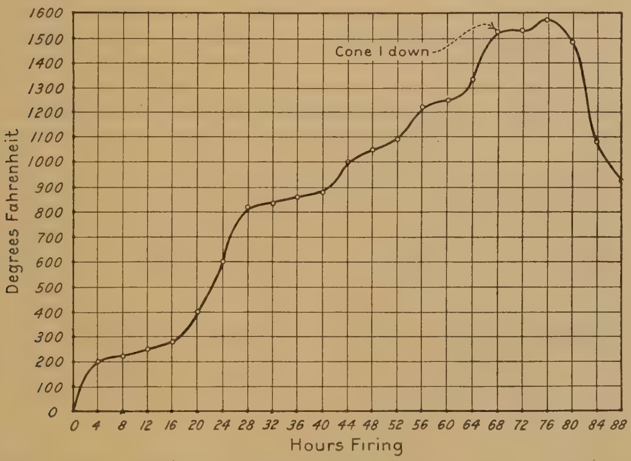

FIG. 2.—No. 2 firing. Paving brick. Cone 1 down. 76 hours to 1570°F. Samples 2, 3, 5, 6, 7, 8.

difficulty found in drying these brick as it was done slowly in the room temperature of the laboratory.

Firing These dried brick were fired in an oil fired round down draft kiln, 4 feet in diameter. The time temperature schedule of these firings as indicated on Fig. 1 brought cone 04 down in 77 hours and the second fire cone 1 down in 88 hours' time. The brick were quartered for trial pieces and these were pulled often to check the progress of the firing. They were particularly accurate and reliable in regard to vitrification, but owing to the fact that they were smaller than the brick did not give accurate information in regard to the oxidation of all of the various shales.

Testing These fired brick were then tested in the standard rattler machine consisting of a drum having 14 sides, into which a charge of shot is placed, 75 pounds of large spherical steel shot and 225 pounds of small shot and the ten block to be tested. It is revolved 1800 revolutions per hour and the loss by weight obtained. The per cent loss is calculated on the original weight of brick.

Results

1. Difficulty in oxidizing this clay prevented a successful test at the present time. It is quite possible to make a paver from this shale as they have been made and used to good advantage; however, to meet the present severe test required of paving brick it would be at quite a disadvantage as compared to other available shales in the state.

2. This material made a paver which had a rattler loss of 24.7% and 24.2% which would be available for medium traffic calling for a loss between 24% and 26%. It would no doubt make a tougher block if there was added more siliceous material as it is very plastic and the block is inclined to be brittle.

3. This material is being used in the successful manufacture of paving block and was used to compare process of manufacture in laboratory with that of commercial conditions. The highest loss obtained in laboratory brick was 23.18% when the absorption was only 0.77%. Other tests where the absorption was higher ran around 19.7% loss. This was evidence that the laboratory method was approaching very close to actual conditions in plant process of manufacture.

4. This shale developed the best red color of all samples and vitrified to a very dense, though glassy matrix, but was entirely too brittle to withstand the rattler test.

5. This shale fired to a dark brown color on the surface having a lighter interior and developed one of the toughest block among the shales tested. The lowest was 18.7% loss and the average for three tests was 20.1%

with an absorption of 7% indicating that with a little harder firing this shale may even show a lower rattler loss. It is evident that this shale would give no trouble in producing pavers the equal of any from competing plants both in and out of the state.

6. This shale has been made into pavers which have been used and given good service in the roads but is just on the edge of the usual requirements of the rattler test. It is quite sandy and the block with lower absorption gave the highest rattler loss namely, 5.1% absorption with 27.9% rattler loss, while the block of 7.2% absorption had a rattler loss of 21.7%.

This block was noticeably regular in the wear during the rattler test and none of the brick broke into halves or chipped off but wore uniformly, indicating that it may be improved by having a better bond in the raw material.

7. This dark shale contains carbon and organic materials which require more attention than was given to it in the first firing of this shale. Due to the fact that this brick had a large blue core in the center, the tests are higher than one would expect it to be when this core is properly oxidized. The rattler loss was 24.7% and absorption 4.8% which is high for medium traffic average but under the maximum permissible loss. This material has given good service in local pavements.

8. This is a light gray shale easily worked on the stiff-mud process, having some organic and carbonaceous material in it which gave little or no trouble in the oxidizing period of the firing. The average of two tests on this shale gave a rattler loss of 20.3% with an absorption of 5.28%. This rattler loss is below general average loss for heavy traffic and no doubt this shale will successfully produce pavers with a margin of safety in regard to the firing of same as it is a very tough material.

9. This brown shale is very plastic and has little impurities which give trouble in the firing, especially in the oxidation period. It fires to a good red color at cone 1, 1850°F, which appears to be a little too low a temperature.

The rattler loss was 23.8% and 24.5% with average of 24.1% and absorption of 4.7%. This rattler loss places brick better than that required for average light traffic. When fired to 1950°F it had a rattler loss of 18.8% with absorption of 2.48% which indicates that this material with proper firing will give an excellent paving block. It would have to be tied rather securely in the setting as it has considerable shrinkage (15% linear) which may cause it to roll or pull when settling or vitrifying.

10. This blue shale was difficult to oxidize and was not successfully oxidized in our firings, hence the presence of a bad blue core in the block. It also had a large linear shrinkage and the rattler loss was 29.9% with 4.8% absorption. While it may be possible to produce a paver with this

material it is not likely that it would be considered seriously for the manufacture of a uniform tough paver.

The part of this experiment referring to the pugging by hand and by wet pan machine showed consistent gain in strength for the machine pugged clay for some materials, while quite the reverse action was obtained for a few others, but the fact remains that a certain amount of pugging is necessary to prepare shale so it will flow through a die of machine satisfactorily, in some instances causing prolonged hand pugging which approached the machine preparation in completeness of work done. There is no question that it is absolutely necessary to thoroughly prepare the shale before forming into ware, so as to get as uniform a texture as possible with a minimum of lamination and a freedom of included air.

Methods of Manufacturing

In connection with this testing of these eleven shales for the manufacture of paving brick an experiment was run on various processes of manufacture to see their effect on the structure and rattler test. Samples of shales were sent to various manufacturers of clay-working machinery and blocks made up on (1) roller expression machine, (2) dry press, (3) soft-mud, and (4) on a new machine which will be called a belt machine. This belt machine consists simply of two belts running between steel sides. They taper towards the discharge end and the clay is fed into it at the open end. This clay is gradually compressed as the space between the belts narrows down to the size of the die, through which issues a column of clay very similar to a stiff-mud column which is of course free of auger lamination. The belts are held to their proper taper by a series of rolls close together. Owing to the fact that this machine has not been released on the market, photographs cannot be shown.

Roller Expression Machine The brick made on this machine were fired in the same kiln alongside of stiff-mud brick made with an auger machine and being made out of the same material and given identical heat treatment will give us a good comparison of the two processes. The block made on the roller expression machine had a rattler loss of 17.2% notwithstanding that there were five stops in running the test due to belt trouble, broken pulley and clutch slipping. The auger machine brick were tested under far more favorable operating conditions of the rattler machine and ran a loss of 19.7% or 2.5% greater loss than that of the block made on the roller expression machine. This machine in order to be a success has to have some arrangement to keep the clay from squeezing out at other places than the die.

Dry-Press Process The shale used in making the block on this process was the same as used on the roller-expression machine, and was found to be too plastic to press well and many of the blocks had pressure cracks in them. A significant factor introduced in this process was the fact that dry-pressing has the same effect on shale as on fire clays, namely, to increase the vitrification temperature as they are much more refractory than the block made by the other processes. Owing to this increase in refractoriness of the dry-press brick they were not nearly vitrified and it is hoped that opportunity will be had to fire them till they are vitrified. The rattler loss was 58.0% and the absorption was 8%.

This process does not seem to offer very favorable factors for making paving brick as most of the shales suitable for making pavers are too plastic to press well and there is a minimum bond produced. The texture is ideal, being free of air blebs and lamination.

Soft-Mud Process Paving brick were made up of a shale from Lehigh, Ia., by the laboratory method and on a standard soft-mud machine and fired in the same kiln until thoroughly vitrified. The laboratory block had a rattler loss of 34.3% and 2.04% absorption and the soft-mud block had a rattler loss of 33%, its absorption being 2%. While both of these losses are entirely too high for a standard paver, still it shows that the soft-mud process compares very favorably with the usual stiff-mud process.

These tests invariably had about half of the brick broken in two and of course this ran the test high, as five unbroken bricks were checked and found to have only a 20.6% rattler loss. This breaking is due to the fact that the shale is exceedingly plastic and became brittle in firing so hard. It did not have the usual amount of siliceous material as used in the manufacture of sewer pipe.

Very plastic shales or clays are difficult to manufacture into brick on the soft-mud machine and the texture of this product is excellent, having neither auger nor die lamination, in fact the only defect is the small amount of air included producing air blebs.

Belt Machine Block The brick made on this machine also had an excellent texture but unfortunately there was no laboratory brick made out of this shale although the deposit is close to a very similar shale which is making a successful paving block. The rattler loss averaged 36% with an absorption of 4.3%. This, of course, is too high for pavers, but may be lowered by firing to a higher temperature. It was quite a disappointment to find a block of such good texture free of air blebs and auger lamination run so high a rattler test and it seems well worth while to make further experiments on this machine.

Effect of Magnesium on Paving Block In a report on paving brick by R. C. Purdy,[1] for the State of Illinois we find the following reference to the effect of MgO in ceramic mixtures:

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[1] Illinois Geol. Surv., *Bull.* 9, p. 243.

(1) Magnesium oxide increases viscosity.

(2) Magnesium oxide gives lower rate of fusion, at least when it is predominating flux.

(3) Clays making good paving block contain larger per cent of magnesium oxide than calcium oxide.

(4) Italians make a tough low-fired porcelain in which magnesium is the only RO or fluxing base present.

The shale from Boone, Ia., was selected for the study of additions of MgO in small amounts, due to the fact that it ran just a little high in the rattler test and seems to be lacking in bond material.

The following is the chemical analysis of this Boone shale and the material used as a source of MgO.[1]

Boone shale	
SiO_2	66.03%
Fe_2O_3	5.27%
Al_2O_3	15.67%
CaO	1.38%
MgO	1.45%
K_2O and Na_2O	1.38%
Loss on ignition	8.94%
	100.12%

Magnesium oxide	
SiO_2	0.62%
Fe_2O_3 and Al_2O_3	0.70%
CO_2	6.87%
CaO	1.95%
MgO	78.85%
Loss on ignition	11.51%
	100.50%

Paving brick were made up with constant additions of above magnesium oxide and were marked 66.05, 66.1, 66.25, 6.2, 66.3, and no difficulty was encountered in drying this set of blocks. They were all given the same heat treatment being fired in the same kiln together. The following curve (Fig. 3) gives the results of tests on these brick, also the exact amount of MgO in each set of brick as determined on the fired brick by chemical analysis. This variation in actual amounts of MgO and that indicated by the number following the clay number (66) which was the per cent added of the material when it was thought to be practical pure magnesium carbonate, is due to the fact that it was mostly the oxide of magnesium.

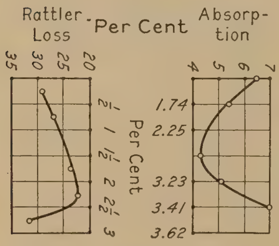

FIG. 3.—Effect of introducing small amounts of MgO from $MgCO_3$ to Boone shale made into pavers.

This addition of magnesium gave a marked degree of fluxing action to this shale and the characteristic red color was changed to a decided buff color similar to that of a No. 2 fire clay. The paver containing 1.74% MgO stood a rattler test of 27.8% loss, absorption 6.5% and 11% linear shrinkage. The color has not changed much, being still a distinct red color. The rattler loss steadily decreased as did the absorption and the linear shrinkage increased as the color changed to a decided buff color with increasing amounts of MgO up to a content of 3.41%.

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[1] As made by G. W. Burke, Chemist.

This paver containing 3.41% MgO has a rattler loss of 22.4%, absorption of 5.1% and total linear shrinkage of 14%.

There is a sharp rise in the rattler loss and absorption of the paving brick made with 3% addition of MgO or the block having 3.62% MgO content, indicating that this has passed the amount which is most beneficial in making the paving block tougher as shown by the rattler test. The rattler loss of this block was 31.6% and the absorption was 7.02%, with 14.5% linear shrinkage. This small per cent of MgO was so bulky[1] that it amounted to about half and half by volume and it would be difficult to incorporate a greater amount of this same source of magnesium and get it thoroughly distributed throughout the shale.

Effects of Colloids The Boone shale was again used to try additions of colloidal material in order to observe the effect on the bond, as indicated by the rattler test. Two colloidal materials were used, one from Beatty, Nevada, and one from Watertown, Ia. One per cent was added to the shale and these were made up into blocks which were fired at the same time as the other brick. They were found to be very much too soft to give a good rattler test and the absorption was high, being 8.5%.

Some grog formed from tile made of shale from Nevada, Iowa, was mixed with 6% of bentonite and made into brick on the plunger machine in the laboratory. These were also found to be underfired at cone 1. A few of these were fired in a small kiln to cone 11 and at this temperature they were thoroughly vitrified. These additions of colloidal material indicate in all three instances an increase in the vitrification temperature as each was entirely too soft at the heat given to the other pavers.

Iowa State College
Ames, Iowa

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[1] Editorial Note: Should have used talc. A small amount (2% or less) of magnesium carbonate would help greatly in forming the ware.

THE CALCULATION OF COAL EXPENSES IN ROTARY CEMENT KILNS[1]

By D. A. Tchernobaïeff

ABSTRACT

The results of the author's experiments upon the heat of formation of cement clinker are given, the formula for calculation of coal expense is deducted. For an easy application of the formula the author gives several tables, and, as an example, calculates the coal expense for the heat balances of C. E. Soper and T. W. Richards.

The Heat of Formation of Cement Clinker

To have a correct heat balance of a rotary kiln we must know the heat of formation of cement clinker.

The heat of formation of silicates and aluminates may be determined by the method of Le Chatelier,[2] consisting in the fusion of silica or alumina with metallic oxides or carbonates added with some fuel (charcoal) in a calorimetric bomb; the mixture is put in a case made of a strip of filter paper and ignited by an iron wire. The difference between the calculated (charcoal, paper, iron wire, etc.) and observed amount of heat ought to give us the sought heat of formation.

By this direct method I have found[3] the total heat of formation of cement clinker (by fusing the raw mixture of a Russian cement mill) to be equal from -308.4 to -309.8 cal. per 1 gram $CaCO_3$ in raw mixture, or the heat of formation excepting the heat of decomposition of $CaCO_3$ (-427 cal. at constant volume, according to Berthelot) from $+118.6$ to $+117.2$ cal. per 1 gram $CaCO_3$.

The direct method may be good in many cases, but we are never sure that we have obtained the sought silicate; the product may not be fused sufficiently, the reaction may remain incomplete; at last the product may be partially crystallized and may partially remain amorphous.

But we can work otherwise. We can fuse first a previously prepared pure, crystalline silicate (or, generally, previously prepared product of reaction to be studied, in this case ready cement clinker) with such a quantity of silica, alumina or any other substance, as to obtain a low melting slag and, secondly, the corresponding mixture of raw materials (in this case, the cement raw mixture) with such a quantity of silica, etc., as to obtain the same slag. The difference of the two observed heats gives us the sought thermal effect.

I determined by this indirect method the heat of formation of the same clinker and found the heat $= +115$ cal.

For two other samples of Russian clinker[4] I found the heat $= +106$ cal. and $+110$ cal.

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[1] Recd. August, 1925.

[2] *Comptes rendus de l'Acad. des Sciences*, **120**, 523 (1895); **122**, 80 (1896).

[3] *Zeits. für angew. Chemie*, **24**, 337 (1911).

[4] *Annales de l'Institut Polytechnique, à Kieff*, **13**, 185 (1913).

For a third sample I found +166.7 cal. This figure seemed to me untrustworthy. To verify the result I made the same experiment, but instead of silica, as usual, I added my clinker and raw mixture with alumina. The observed amounts of heat were quite different, but the difference gave me the same figure, namely, +169.4. This proves the correctness of the method; as to the difference between the results for this and other samples of cement, I found it explained in an abnormally great amount of organic matter.

For a quite correct thermal balance we should therefore determine the heat of formation in every particular case experimentally; for an average balance I assume the average heat +110 cal. or the total heat = +110 − 443 = −323 large calories per 1 kilo $CaCO_3$ (−433 = heat of dissociation of $CaCO_3$ at constant pressure according to Berthelot) or −735 large calories per 1 kilo CO_2 in raw cement mixture.

Average Heat Balance of a Rotary Kiln

In calculation of an average (approximate) heat balance I assume the initial temperature of raw materials, air and fuel = 0°C. I take no notice of heat losses in dust and ready clinker (its temperature being only about 75°C in modern kilns). Some of these errors being positive and others negative, the total sum of errors can be neglected. I take the average composition of air-dried mixture as follows: loss of ignition 36.5%; CO_2 content 33.5%; water = 36.5 − 33.5 = 3%.

The quantity of added water (wet process) $h\%$ or $\frac{h \times 100}{100 - h} = m$ per cent of air-dried mixture.

As I have demonstrated in another place,[1] the volume of gases of combustion of 1 kilo coal may be approximately expressed:

$$D = 1.11 \frac{Q}{1000} + 1.07(n-1)\frac{Q}{1000}$$

where

D = the volume of gases at standard conditions in cubic meters
Q = the upper heat of combustion of coal
n = the ratio of air actually admitted to air theoretically necessary for complete combustion.

The excess of air I take 5%; $n = 1.05$. The specific heat of gases is taken according to Holborn, Hennig and Pier.[2]

At these conditions we have the following heat balance for 100 kilos of clinker:

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[1] *Schriften des Kiewer Instituts für Volkswirtschaft,* **1,** p. 1 (1923).

[2] M. Pavloff, *Jour. of the Russian Metallurg. Soc.,* **1,** 421 (1912).

Heat input. The coal expense = $x\%$, the lower heat of combustion Q'. . . . . $Q'x$ cal.

Heat output.

I. The heat of reaction is easy to calculate. . . . . .38,779 cal.

II. The heat of evaporation of water at 0°C, 607 cal. per 1 kilo, according to Clausius, gives us. . . . .$956m + 2868$ cal.

III. The loss of heat in waste gases at the temperature t°C:

(1) With CO_2 and H_2O vapor from raw mixture:

with H_2O. . . . . $0.0875\,(m + 3)a$ cal.
with CO_2. . . . . $1.199b$ cal.

where a and b are the amounts of heat to warm 1 kilogram-molecule of H_2O and CO_2 from 0° to t°C.

(2) With combustion gases: The loss of heat with combustion gases

$$D.W.x \text{ cal.}$$

where D is the volume of gases per 1 kilo of coal and W the amount of heat to warm 1 cubic meter of gas at standard conditions from 0° to t°C. The values of W at 5% exceeding air are given in Table I.

TABLE I

$t°$ =	200	300	400	500	600	700	800	900	1000°C
W =	66	100	134	169	205	241	279	317	355 cal.

IV. The loss of heat by convection and radiation at experimental balances is usually calculated by difference.

As a first approximation I assume it is directly proportional to the surface of the kiln and the temperature of waste gases and inversely to the thickness of fire-proof wall of the kiln. From correct balances for some Russian and German kilns I have calculated that the loss is approximately:

$$\frac{S}{d.B}\,(20.9t° + 5688) \text{ cal.}$$

where S = the surface of the kiln in square meter
d = the thickness of the wall in meter
B = the quantity of barrels (170 kilos each) per day
$t°$ = the temperature of waste gases

As the sum of items of output is equal to the input, we get the necessary equation, and, by solving it, we obtain the following expression for coal expense:

$$x = \frac{1}{Q'-DW}\,(41647 + 0.2625a + 1.199b) + \frac{1}{Q'-DW}\,(956 + 0.0875a)m + \frac{1}{Q'-DW}\cdot\frac{S}{d.B}\,(20.9t° + 5688)$$

The first member of this expression gives us the coal expense at the dry process ($m = o$) and at the absence of convection and radiation losses.

The second member, the coal expense to evaporate the water and to warm the water vapor at the wet process.

The third member, the coal expense to compensate the losses by convection and radiation.

The expression $Q' - DW$ is the heat given by every 1 kilo of coal to the kiln as DW is the lost heat in combustion gases.

The Tables to Calculate the Coal Expense

To facilitate the application of the deducted formula, I have calculated the Tables II, III and IV giving the values of separate members of the formula at different temperatures of waste gases and different contents

TABLE II

THE VALUES OF THE FIRST MEMBER

$t°$ = the temperature of waste gases

$t°$ =	100	200	300	400	500	600	700	800	900	1000°C
I member =	6.17	6.64	7.18	7.78	8.46	9.24	10.14	11.19	12.40	13.82

TABLE III*a*

THE VALUES OF MEMBER II (WET PROCESS)

$t°$ = the temperature of waste gases, $h\%$ = content of water

$t°$ = $h\%$	100	200	300	400	500°C
30	6.33	7.06	7.86	8.78	9.79
31	6.63	7.40	8.24	9.20	10.26
32	6.95	7.75	8.64	9.64	10.75
33	7.27	8.11	9.04	10.09	11.25
34	7.60	8.48	9.45	10.55	11.77
35	7.95	8.87	9.88	11.03	12.30
36	8.30	9.26	10.32	11.52	12.85
37	8.67	9.67	10.78	12.03	13.41
38	9.05	10.09	11.25	12.55	14.00
39	9.44	10.52	11.73	13.10	14.60
40	9.84	10.98	12.23	13.66	15.22
$t°$ $h\%$	100	200	300	400	500°C
41	10.26	11.44	12.75	14.23	15.87
42	10.69	11.92	13.29	14.83	16.54
43	11.13	12.43	13.84	15.45	17.23
44	11.60	12.93	14.42	16.09	17.94
45	12.08	13.47	15.01	16.76	18.68
46	12.57	14.02	15.63	17.45	19.45
47	13.09	14.60	16.27	18.17	20.25
48	13.62	15.20	16.94	18.91	21.08
49	14.18	15.82	17.63	19.68	21.94
50	14.76	16.46	18.35	20.48	22.84
60	22.14	24.69	27.52	30.78	34.25

TABLE IIIb

THE VALUES OF MEMBER II (DRY PROCESS)

$t°$ = the temperature of waste gases, $h\%$ = content of water

$t°$ = $h\%$	500	600	700	800	900	1000°C
5	1.20	1.34	1.51	1.70	1.92	2.18
6	1.46	1.63	1.83	2.06	2.32	2.64
7	1.72	1.92	2.16	2.43	2.74	3.12
8	1.99	2.22	2.49	2.81	3.17	3.60
9	2.26	2.53	2.83	3.19	3.60	4.09
10	2.54	2.84	3.18	3.58	4.05	4.60

TABLE IV

THE VALUES OF MEMBER III AT $\frac{S}{d.B} = 1$

$t°$ = the temperature of waste gases

$t°$ =	100	200	300	400	500	600	700	800	900	1000°C
Member III	1.12	1.49	1.87	2.31	2.79	3.33	3.94	4.65	5.45	6.39

of water at the wet process. For the third member the values are given at $\frac{S}{d.B} = 1$ and must be calculated, in every particular case, as indicated, lower.

As a ground of calculation coal is taken with $Q = 7500$ cal. and $Q' = 7250$ cal. Coal expense is directly proportional to the expression $\frac{1}{Q' - DW}$. With an insignificant error we can in many cases take it proportional to the expression $\frac{1}{Q}$.

To show the use of the tables, I will calculate the coal expense for the kilns of the heat balances of E. C. Soper and T. W. Richards.

The Balance of E. C. Soper:[1] The raw mixture contains 53% of water ($h = 53\%$). Coal expense = 48.06%; the heat of combustion = 5608 cal. Temperature of waste gases = 236°C.

The length of the kiln = 30.38 meters, the diameter is 2 m. The thickness of the wall is unknown; I assume it to be 0.2 m. The kiln gives 166 barrels per day. Hence $\frac{S}{d.B} = \frac{\pi . 2 \times 30.48}{0.2 \times 166} = 5.77$. We shall calculate the coal expense for the temperature 200° and 300° and then find the expense at 236° by interpolation.

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[1] C. Naske, "Die Portland zement Fabrication," Russian edition, p. 149 (1913).

Temperature	200°	300°
Member I	6.64	7.18
Member II	18.96	20.08
Member III	5.77 × 1.49 = 8.60	5.77 × 1.87 = 10.79
The sum	34.20	37.99

For $t°$ = 236°C we obtain:

$$34.20 + (37.99 - 34.20).\frac{36}{100} = 35.56\%$$

And for the heat of combustion 5608 cal.:

$$\frac{35.56 \times 7500}{5608} = 47.63\% \text{ instead of } 48.06\%$$

The Balance of T. W. Richards:[1] The excess of air is unknown, but, as the gases contained 0.2% CO, it cannot be great and we commit no appreciable error by calculating for an excess of 5%.

The temperature of the clinker was 1200°C, and the loss of heat calculated by Richards is as great as 100,500 cal. per 100 kilos of coal or 345 kilos of clinker, hence the loss per 100 kilos of clinker is 29,000 cal. To compensate this we must burn $\frac{29,000}{Q'-DW}$ kilos of coal more, namely 6.01 kilos, at the temperature of waste gases 800°C and 6.46 at the temperature 900°C.

The coal expense was 28.98%; the heat of combustion according to Dulong's formula (calculated by me) = 7.395 cal. The temperature of gases = 820°C. The length of the kiln is 18.29 meters, the diameter, 1.829. I take d = 0.2 m. The kiln gives 233 barrels per day by dry process. Hence

$$\frac{S}{d.B} = \frac{\pi 1.829 \times 18.29}{0.2 \times 233} = 2.25$$

Temperature	800°	900°
Member I	11.19	12.40
Member II		
Member III	2.25 × 4.65 = 10.46	2.25 × 5.45 = 12.26
The loss in hot clinker	6.01	6.46
The sum	27.66	31.12

At the temperature 820°C: $27.66 + (31.12 - 27.66)\frac{20}{100} = 28.37\%$.

At the heat of combustion 7395 cal.: $\frac{28.37 \times 7500}{7395} = 28.75\%$

T. W. Richards gives 28.98%; one cannot desire a better coincidence.

KIEFF
POLYTECHNICAL INSTITUTE

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[1] *Jour. Amer. Chem. Soc.*, **26**, 80 (1904). C. Naske, *Zeits d. Vereines Deutscher Ingenieure*, p. 1354 (1905).

PRINCIPAL REFRACTORY PROBLEMS OF THE MALLEABLE CAST IRON FOUNDRY

By H. A. Schwartz[1]

ABSTRACT

The paper covers a brief description of the necessary conditions under which fire brick are used in air furnace melting, and outlines some of the elementary relations between fuel economy and refractory economy, including loss of use.

It has suggested as a ceramic problem, that the principal fields for improvement lie in developing refractories more resistant to slags for side walls, and more resistant to changes of temperature for furnace roofs. It is further suggested that unless higher refractoriness can be secured, the field for the use of heat insulation in such furnaces is probably negligible. The very refractory materials now known, seem to fail, due to a lack of resistance to thermal stresses.

This paper is to be considered as a brief summary of some factors affecting the performance of fire brick in air furnace melting. Its brevity and the fact that most of what the writer will have to say deals with metallurgy, and not ceramics, is merely an expression of his ignorance in the latter field.

It is quite obvious that the principal interest of ceramists in a metallurgical subject will be the opportunities of applying, within their profession, data gathered by the user of their material toward the end of an improvement in refractories, and the general benefit of all. Leaving the reader to make for himself the proper applications, the following discussion has been prepared.

In air furnace melting we are confronted with the necessity for combustion conditions, such that the final products will contain little, or no free oxygen, and a few per cent of carbon monoxide. The reason for this requirement is deeply rooted in the chemical equilibria between the gas and liquid phases in contact in the furnace. It is not capable of modification for any purpose whatsoever.

Under these conditions, the maximum flame temperature is possibly 3200°F, as actually measured in commercial furnaces. The temperature of the face of the furnace walls will be that at which heat input, by convection mainly, is balanced by losses by conduction outward and radiation from the furnace structure. This means in practice, perhaps 3000°F, the resulting metal leaving the furnace at temperatures about 2600°F.

If now the thermal engineer seeks to minimize radiation loss by using very thick walls, the inner face of the wall grows hotter, since the cooling action of the furnace exterior has diminished. He thus buys fuel economy at the expense of refractory economy.

In furnace roofs of "bungs," a thickness of $4^1/_2$ inches is almost the universal standard. Probably this has been arrived at as the best balance

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[1] Recd. Jan. 26, 1925. Presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, Feb., 1925. (Refractories Division.)

between brick, labor and fuel economy. In side walls, thicknesses from 18 to 9 inches are in use. The former fail, in the beginning, quite rapidly in the writer's experience. Very probably 9-inch walls would be ideal if there were not a desire to break joints at least once in the thickness of the wall. As a matter of fact, were it not for the mechanical instability of very thin walls, a thickness of from $4^1/_2$ to 6 inches might be maintained indefinitely by some method of exterior cooling.

The best economy in both fuel and brick, with which the writer is familiar, was obtained on furnaces with 12-inch walls. Heat insulation would seem to hold out no promise of merit, for it would result, probably, in the rapid destruction of the inner refractory linings. The heat capacity of furnace structures is also of importance. The conductivity of clay refractories is not so great but that considerable time elapses before they reach their final equilibrium temperatures. If the structure be allowed to cool over night, they actually will not ever reach equilibrium in service, and hence, will survive more hot hours than when continuously operated. Air furnaces operated twenty-four hours a day have required major repairs in less than a week, while, when operated sixteen hours a day, they would require much less repair after two weeks.

Erosion by flue gases is an important source of wall destruction. The flame must move sufficiently rapidly through the hearth to produce the circulation in the bath required for quick heating. It carries with it a spray of slag and iron particles, which flux the roof and walls, and the friction of the hot gases drags this softer material off and carries it along. Wherever constrictions occur, or parts project sharply into the stream of gas, rapid cutting occurs.

Most furnaces use "top blast" and if these streams of air are so directed as to strike a wall, the brick is very rapidly cut out by a combination of melting and erosion.

Somewhat fantastic roof forms were formerly rather common, and it was also thought that the top blast would force the flame away from the roof. It is very doubtful whether either arrangement has any merit whatever, and the writer is committed to a roof which in profile is nearly straight, but dips down toward the stack.

The character of the fuel is also of importance. Most air furnaces are grate fired, using forced draft. Most coals, so fired, blow particles of coal, coke and ash up into the gas stream, which impinge on the roof over the fire box. Depending on the character of the ash, it may flux the brick and cause roof failure, or it may stick as a spongy mass, and protect it.

Coal also differs in the time required for its gaseous decomposition products to unite with the air supply. If this time be very short, a high temperature may be realized before the gases strike the fire box roof, and much damage done. It is one of the functions of the top blast to avoid the possibility of complete combustion, and hence maximum temperature occurring before the flame has come into contact with the charge. With pulverized coal there is an advantage in that the burning mass travels always along the length of the furnace, and hence need not impinge on the walls or roof at its point of maximum temperature.

In the early days of oil burning, such hot localized flames did a good deal of destruction to brickwork, although in later installations this has been largely overcome. There is now a distinct feeling that both pulverized coal and oil are less destructive to furnace linings than is hand fired coal. Whether the point is capable of rigid proof is somewhat doubtful. Some indirect effect through chemical action may also be expected, for any system which uniformly regulates the combustion, will avoid accidental over-oxidation of the charge. The products of such oxidation are very destructive to clay brick.

The writer has in the past touched upon the chemical action of slags. During the progress of each heat the slag changes progressively from molten Fe_3O_4 to acid ferrous silicate, resulting in a serious problem to the ceramic chemist, who wishes to minimize its fluxing action on his product.

In furnace roofs we are confronted with mechanical difficulties. Too round an arch results in an unfavorable flame distribution, too flat a one imposes too high stresses on the "bung frame."

The life of bungs is enormously influenced by their mechanical rigidity. It is within our knowledge that a mechanically more stable design more than doubles bung life. Bungs are used 9, 13, 18 and 24 inches wide. Where crane service is available the 24-inch bung is much the most economical, although the 13-inch size is, perhaps, the commonest. Only considerations of the weight which can be handled without abuse should limit bung width. If the brick are to be held firmly, they must be strong, not cracking under pressure. Also, since variations of temperature are unavoidable, they must resist this condition.

Conclusions

The temperature and chemical composition of flue gases, the composition of slags, and the temperature fluctuations due to charging are virtually fixed quantities which neither the producer nor the consumer of brick can alter. The method of firing, the fuel chosen, the design as to form and material of the furnace walls, are within the limitations of available material within the metallurgist's choice.

The melting point of the refractories, having regard also to the fluxing action of slags or ashes, now sets some limit on the degree to which he can reduce radiation losses. Were there a chemically inert refractory of a melting point above the theoretical temperatures of combustion of his fuel, he might thicken his furnace walls and economize on heat. Such thickening would, perhaps, have to be in the form of increase in number of layers of refractory to avoid increases of stress due to greater thermal gradients in individual shapes. On the other hand, were the brickmaker relieved from the need of considering chemical destruction of his product, the admissible temperatures would at once be increased.

Some of the artificial refractory minerals, spinel, sillimanite, etc., hold great theoretical advantages. In the present state of the art they seem to lack resistance to thermal stresses. If the problem be viewed merely as a reduction in the amount of refractories used, and in the interruptions of service for repairs, a thin walled, artificially cooled furnace might furnish the solution at an undetermined increase in fuel costs.

It is very doubtful whether all the variables here alluded to could be combined into an equation from which, given the unit costs, the most economic practice might be calculated. It is much more likely that the operating executive will continue to arrive at his results by a process of trial and error in an attempt to find the fuel, refractory and design which reduces his cost for labor, material, overhead and losses due to interruptions in service to a minimum.

In the present state of the art, it is probable that the ceramist's efforts may be most profitably applied in the direction of improving the resistance of side wall brick to the chemical action of slags and of bung brick to mechanical destruction by thermal stresses and perhaps the stresses applied by the bung frame. So far, the best solutions seem to have been based on the making of very dense brick for the former, and coarse, open brick for the latter.

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REFRACTORY REQUIREMENTS IN THE GRAY IRON FOUNDRY[1]

By Richard Moldenke

ABSTRACT

The author calls attention to the lack of information on foundry refractories on the part of both foundrymen and makers of refractory materials. The applications of these materials in foundry practice are enumerated, and the requirements detailed sufficiently to enable the manufacturer to select the proper grades of brick and clay for cupola and air furnace operation, as well as for the lining up of ladles.

Introduction

The refractory requirements of the iron foundry are of prime importance in that industry, as will be understood by recalling that from the melting of the iron mixture to the removal of the cold castings from the foundry floor all containers for the molten metal must withstand extremely high temperatures. And this is the case whether the castings be of any form of iron—gray iron, malleable cast iron, which in its original form is white cast iron, and steel.

While the foundryman is perfectly aware of the fact that insufficiently refractory materials are the cause of much loss to him in the melting, pouring and subsequent cleaning operations, neither he nor the producers of these materials are always sufficiently familiar with the subject to know just what to do. Further, the force of habit is such that foundrymen will keep on digging clay for daubing their ladles on their back lot, and dealers in refractory materials will not study the co-related foundry problems involved in order to supply what is required. Nor will they follow the situation on the ground, and thus familiarize themselves with the processes used so that they may put their fingers on weak points, and help make the necessary corrections.

The result of this situation is that the foundrymen themselves, through specially constituted committees of competent bodies, are taking a hand in the game of refractories, and we now have a thorough investigation of the molding sand problem going on in America, with work along the same lines prosecuted in Germany. Also, a remarkable development of loose refractory materials for foundry work going on in Germany, with similar studies in the way of high temperature bonds by the makers of refractories under way here. It is purposed, in what follows, to itemize the foundry processes involving the use of refractories and to discuss the requirements in sufficient detail to allow the maker of refractories to draw the necessary deductions.

Foundry Refractories

Cupola

The refractories used in the lining of cupola is in importance next to the molding sands.

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[1] Recd. Dec. 15, 1924. Presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, February, 1925. (Refractories Division.)

Disregarding the crucible as obsolete in the iron foundry, leaving the open-hearth and the electric furnace for discussion under refractories for steel castings, there remain only the shaft or cupola furnace and the reverberatory or air furnace to be considered here. Gray iron—as also white cast iron, is melted in these two types of furnaces in enormous tonnages and under temperatures and other physical and chemical conditions which make it highly important to use the proper refractories in their right places. The cost accounts of foundries make special provision for fire brick and clay used in cupola and ladle repairs and maintenance, and where much and very light steel scrap is charged—as in making sash weights—the item of refractories is a heavy one.

The cupola, which melts the bulk of the iron used for gray iron castings, is a cylinder of refractory material held in place by a steel shell, into the top of which are charged alternate layers of metal and fuel, with air blown through from below. Iron melts in a comparatively small zone about two feet above the blast entrance and is collected in the crucible of the shaft to be tapped out and poured into molds. The operation of melting is as continuous as may be wished, subject to the lasting of the refractory lining at the melting zone.

The Charging Zone There are three requirements to be met by the lining. First, as the metal is charged the lining must be able to stand terrific abuse, for there is to be considered not only the blow of the jagged-edged heavy pig of iron as it is thrown in, but also the abrasion of a rigidly packed gridwork of iron tools—as it were—cutting their way along the lining as they descend. The temperatures themselves are not very high here, though still high enough to require refractories instead of a metal lining, as otherwise the steel shell will buckle and endanger the structure. Coarse-grained, friable fire brick are out of question here, and there is indicated a hard, dense, fine-grained brick still refractory enough to hold the heat from interfering with the life of the shell.

Above Melting Zone As the charges descend to fill the place of those melted away, they become heated more and more until arriving at the melting zone the metal softens and drops away. Hence, one or two feet above the melting zone top—depending upon how much blast finds its way up along the lining—there is very little abrasion but the temperatures become important.

The Melting Zone When the melting zone is finally reached and the iron runs from the melting charge in drops and little rivulets, the refractory lining must not only stand the maximum temperature of the superheated molten metal (for the drops of metal have little chance to become hotter than they are when they part from the pig and scrap) but the much higher temperature of the fuel bed it is in contact with. That only the very best of refractories will stand up here is shown by the fact that when poorer grades of brick are used even a comparatively short run will melt out the material to a point endangering the cupola. In such cases the melting zone may have to be refined after every heat. Hence the second requirement of high refractories.

Slagging Action of Charges

So far as refractoriness is concerned a high grade, coarse grained and perhaps friable brick might stand all right in the melting zone and below it right to the bottom of the cupola, were it not for another factor to be considered. This is the slagging action of the charges. As the coke used for fuel burns away, at least 10% of its weight remains behind as ash. As the pig iron melts, if sand-cast, there will remain some sand and gravel; similarly the burnt molding sand on the gates and sprues of the castings made the day before, if these be not cleaned by rumbling. All this material remains as the molten iron runs away from it, and is picked up by the calcined limestone arriving at this point at the same time. Hence, a slagging action is exerted upon the lining already under an extreme of temperature. It is highly important therefore, that the refractory lining be so constituted that as few joints as possible be searched out and entered into by the slag at hand. Hence the disadvantage of coarse-grained refractories here also. The third requirement of cupola refractories, therefore, is a high resistance to slagging action.

Repairing of Linings

Above Melting Zone

In general, the attempt is made to combine all three requirements in the same brick, as it does not pay to differentiate in the classes of brick used for the lining above and below the top of the melting zone except in the larger foundries running a number of cupolas constantly. Once the upper portion of a cupola is lined with a good strong, fine-grained fire brick and the charging door still has an apron covering that part of the lining, with perhaps some cast iron blocks inserted in the lining at danger points opposite the door, nothing need be done in the way of repairs for many months of steady service.

Melting Zone

The portion of the lining at the melting zone and below this is quite another matter. Here, repairs are obligatory after every heat. If charging has been done properly the cutting action of melting iron and slag should be confined to a belt from six to nine inches wide, situated from 16 to 18 inches above the top of the tuyères at its lower border. If the charging system was improperly arranged, this belt may begin six inches above the top of the tuyères and extend three feet upward. Depending upon the quality of the brick and the handling of the cupola, this cutting into the lining may be but half an inch at its worst, but where periodic metal charges might have consisted of large-surfaced salamanders the deflection of the hot gases against the lining in going upward must of necessity have cut deeply into the brickwork.

Daubing

Repairs are performed ordinarily by chipping off adhering material from the cupola run down to the slag glaze on the brick, and then daubing up the lining to a reasonable condition of fitness for the next run. The desire, of course, is to bring the lining back to the original dimensions, and hence, where the cutting has been deep there are inserted into this daubing pieces of fire brick, or even whole brick, as also large flakes of mica schist.

The point of interest to the maker of refractories is the composition of the "daubing," which consists of clay and fire sand so proportioned that there may eventuate a minimum of shrinkage. The fire sand used is usually good enough so far as refractoriness is concerned, but the clay in question is often lamentably wanting in this respect. Since this daubing is generally the same material used to prepare the ladles for containing the molten metal to be poured into molds, these items can be taken up together.

In daubing up the cupola with poor clay the consequences are very disagreeable, particularly as the melter who puts up with such poor material is usually a poor workman too. Instead of chipping out the cupola so that some proportion, at least, of the lining surface at the melting zone is cut clear down to clean brick, he will simply rip away projecting scoria and then proceed to daub on the clay-sand mixture, if necessary in successive layers, until the desired thickness is reached. When this thick mass—with enclosed brick often three inches in spots—right in the hottest position, becomes incandescent in the early part of the heat, and the slag coating of the lining it rests against softens, the whole of the daubing slides down and must be slagged away or bung up the cupola badly, besides offering the badly cut up melting zone of the lining to further attack. The writer has known of cases where a wheelbarrow full of daubing had thus slipped down daily to be slagged away at the cost of much coke and limestone, and the melting zone of the cupolas required relining to the shell every week. It cannot, therefore, be emphasized too strongly that none but the most refractory clay—of good fatness—should be used about a foundry, as it always pays good returns.

New Method of Lining

There is a new situation coming forward in the foundry in the way of lining up cupolas and repairing such linings. It is a German development in line with many of their forced economies. Fire sand is mixed with suitable clay and rammed directly into place in a cupola between the shell and movable forms of the desired interior lining diameter. The lining thus becomes a single mass, and when of proper composition, dried out slowly and heated carefully, is said to be as good in practice as a brick lining, and of one-thirtieth the cost, over there. This new material, called "Stampfmasse," which translated can either mean a material to be rammed or "loam" to be rammed, is now sold in enormous quantities for all kinds of furnace linings, being in effect raw fire brick; and is now even put up into blocks, half blocks, and quarter blocks of the desired diameters of cupolas, under hydraulic pressure, to be tamped together with loose material into one solid mass. Once a slag glaze is formed on this lining, it answers just as well as regular brick, and can be patched up without any difficulty. Ground fire brick can be used in place of fire sands, just as is the case with our high temperature cements. Inasmuch as a development of this kind, which is capable of considerable economy in foundry melting operations, is bound to be followed up here shortly, it would seem well for manufacturers of refractories to anticipate the demand by studying the situation from the American founders' standpoint and getting in position to furnish both bonding material and refractory fillers in quantity and at entirely different prices than are the rule today for high temperature cements. Otherwise this coming business will get into other hands.

Refractories for Ladles

If there is any place in the foundry where the most refractory clay should be used it is for the repair of the melting zone portion of the cupola, as this registers the maximum temperatures dealt with. Again, if there is any place where it is important to retain a high degree of heat as long as possible, it is in the ladles carried about the foundry to pour off the molds. And yet, just here is where carelessness is the rule, for if a foundryman can get access to a local clay bank he thinks will serve his purpose he considers himself fortunate. If the clay is only fat enough, its refractory qualities are hardly considered. Hence his ladles must be lined very thick to prevent premature skulling and molds misrun and short poured because of cold iron, not to consider the reduced weight of molten metal carried. The use of a very refractory clay with fire sand in lining up the smaller ladles of the foundry, and for daubing the large ladles lined with fire brick, will mean a comparatively thin wall between the molten iron and the ladle steel to check radiation outward and consequent retention of heat where it is needed. It looks very bad to see the men go about with ladles showing red spots once they have been filled a few times.

Core and Annealing Ovens

There remains but to mention refractories used for furnaces as used in the foundry. Core and annealing ovens, requiring merely heat resistance —light in the first case, just below melting iron in the second—are lined with the cheaper product of the high grade refractories plants, or usually the "seconds" of the highest class brick. It is only when an air furnace has to be used in a foundry that this matter must be considered seriously, and then it will be found that abrasion plays no important part; but resistance to high temperatures, and also strong resistance to slagging action are essential. Not only the slag line of the furnace hearth must stand up against corrosive influences, but sides and roof are peculiarly subject to slag and iron particles thrown up against them when the bath is in violent ebullition. Hence, a very fine-grained refractory clay brick is preferable where roof and sides are close to the bath. Where the roof is high, as in the case of the usual air furnace of a gray iron foundry for chilled rolls, or where very large pieces of scrap must be melted, the roof brick can be of coarser grain, provided the refractoriness is everything that can be desired.

In conclusion, the writer wishes to emphasize the fact that even though gray iron has a lower melting point than steel, this should not mean that lower grades of refractories will do for it. The melting zone of a cupola is the hottest known except that of the electric furnace. And even in the lining of ladles, an unnecessary slight drop in temperature of molten iron —through a poorly refractory clay—say for pouring radiators, will result in lost castings to such an extent that the money loss is hundredfold that of the additional cost of a good clay used for daubing material. Hence, "the best is only good enough" even in the gray iron foundry.

WATCHUNG, N. J.

Discussion

M. C. BOOZE: The Refractories Manufacturers' Association has had for several years an industrial service committee and one of the sub-committees has been on the refractory for foundry use. The purpose of the industrial survey work is to get data on refractories. We have attempted from time to time to get in touch with the Foundrymen's Association to get data and I believe we have failed to get answers to letters.

It is stated in the paper that the "rammed in" lining is coming into use. It seems like bad practice to me.

F. J. KENNEDY: I am connected with the Foundrymen's Association. The average foundryman does not have enough available reading matter on this valuable subject for his information. We know there is information available and we are planning and hoping that we can now have a joint committee to distribute this information to us. There are a few plants which have research departments and they solve their problems but the great trouble lies in the educating of these men so that they will be up in the matter.

As a rule the foundryman uses the nearest available and cheapest material. It is for us to get more papers and more information through the press as an educational matter.

A. F. GORTON: I agree with the last speaker that the foundrymen have come forward with some of the results of experiments with their refractories. The refractory people are not in position to experiment directly but the foundrymen are. There are many important questions to be investigated, for instance, molding sand, core sand in particular, lining of the cupola and the ladle. Experimental work is being carried out on molding sand and possibly on core sand. The core sand for malleable practice is possibly more important than the molding sand and a whole lot of work remains to be done on synthetic molding sands. We are doing some of that work ourselves and I would like to hear from these foundrymen who are conducting such investigations.

Dr. Moldenke speaks of the use of cheap clay and its value in the foundry. A similar case happened at our foundry. They got into trouble one time and wanted to get some brick in a great hurry in order to line the melting zone and they were given some zircon brick. They did not stand up at all but slagged down and ran like so much water. Probably the iron content of loam and cheap clay is the reason for the superior service of such materials when in contact with the molten metal.

W. G. OWENS: I believe in some of the smaller foundries that misuse of the brick has something to do with failures. Perhaps they should have ordered three grades of brick instead of using one grade in various zones of the cupola, for lining the ladles and for other purposes.

We know that the big steel plants, or the big blast furnaces would not think of using the same grade of brick in various zones of their blast furnaces and while the cupola is much smaller foundrymen could get much better service from brick in the upper zone if they would use hard, dense brick.

I know of a foundry that was using a high grade brick in the iron ladles and suggested they were using a too high grade brick and they made the substitution of a cheaper brick. They got more than 100% more life out of the cheaper brick, which cost them about $30 instead of $45. One trouble with the small foundries is that they are using just one grade of brick instead of using three grades of brick. Brick must be chosen that are best suited for the particular service encountered.

R. MOLDENKE: Referring to attempts on the part of committees on refractories to get information from foundrymen on this subject, I fear that these users of refractory materials know so little about the subject, other than that they observe the results, that questions sent out simply cannot be answered by them. Even in the few laboratories in foundries (compared with the great number of the foundries themselves) there are not many men familiar with the manufacture of refractories. Otherwise, there would not be so much trouble and loss to contend with as the result of poor or unsuitable materials. Only close coöperation and continuous testing of the several products of the refractories establishment right in the cupola and ladles of the foundry will give the desired information. Unquestionably differences in charging and melting methods, as well as the character of the pig and scrap charged, not to speak of the fuel and fluxes used, will make differences in the reaction upon the refractories. It is true that good cupola block very closely laid will give better life than any lining that can be shoveled in loosely and rammed between an interior form and the cupola shell. However, the comparatively high cost of refractories in Europe has compelled this new method of firing the lining in place. Since cost data have shown the method to be one-thirtieth the cost of putting in brick or blocks over there, it is but natural that the method will come here eventually. It would have come into use here some time ago had not the selling price of the so-called "high temperature cements" which form the basis of the method been held so high. The expansion of the ramming up method in Europe to the great extent it has assumed would indicate that the results must be eminently satisfactory.

The instance mentioned of too high a grade of brick used in lining up a ladle is undoubtedly correct in that a cheaper brick gave longer life to the lining, but it should not be forgotten that cheaper brick are usually less refractory than the best qualities. This means a quicker cooling of the metal during transit and waiting to be poured. This, in turn, means more lost castings. So that it is not the getting of inferior grades of brick that should be considered insofar as the life of a ladle lining is concerned, but the character of the very best brick to be had to do the work properly, that is, the fineness of grain structure, resistance to slagging action, etc.

L. C. HEWITT: Relative to the conditions present that might affect the life of the block, it would be of interest to develop whether or not the majority of cupola slags are acid or basic, and what is the exact influence of fluxes such as limestone and fluorspar upon the lining. It has been my understanding that the majority of cupola slags are, perhaps acid in character but that slags in the same cupola on the same day may change from acid to basic, as fluxes such as limestone are added, depending upon quantity used.

Relative to the prime requisites of melting zone block, refractoriness, freedom from impurities, density and chemical composition as affecting resistance to slag action would seem to be the chief factors.

It would be of interest to learn whether or not the most desirable silica-alumina ratio of melting blocks has been determined or whether it is possible to determine such a ratio which would be applicable to all types of cupola service, considering, of course, the melting zone proper.

THE EFFECT OF VARIATIONS IN CUPOLA PRACTICE ON THE LIFE OF THE REFRACTORY BLOCKS[1]

By James T. MacKenzie

ABSTRACT

This paper discusses chemical, mechanical and physical influences acting on cupola linings and their combined effects. A brief description of common practice in lining, preparation and charging of the cupola is followed by a discussion of the effect of the daubing practice, the character of fuel, metal, flux and blast. The principal point of the paper is the injurious effect of oxidation resulting from thin or rusty scrap and from too high velocity of the blast.

The life of the refractory lining of the cupola furnace depends on its successful resistance to three direct influences discussed as follows:

1. Chemical The solvent action of the slag and the chemical union of the basic oxides of the charge with the silica of the lining. The action of iron oxide at high temperatures in the presence of molten iron is more severe than is commonly known, a very illuminating experience being the search for a crucible material described by Messrs. Tritton and Hanson in a paper on "Iron and Oxygen" read at the Fall Meeting of the Iron and Steel Institute (1924). The authors state that crucibles of silica, china clay and alundum were tried, "in none of which was it found possible to hold molten iron containing much oxide for more than a few minutes owing to the rapid attack of the pots by the oxide."

2. Mechanical The actual grinding off of the blocks by the descent of the charge and the ascent of the gases carrying suspended particles of abrasive or corrosive materials. Sharp corners on large pieces of coke and iron are particularly destructive in the stock, while sand and fine coke are preëminently abrasive when caught in the blast. Slag is also blown considerable distances up the stack and freezes onto the brickwork.

3. Physical The actual melting off of the ends of the blocks in the melting zone where temperatures of 1600°C and over are encountered. The spalling of the blocks and rupture of the mortar joints when subjected to changes of temperature incident to intermittent operation. Abuse in operation such as rough treatment of the lining in chipping, drying and charging.

It is evident that these three forces are all at work together and each one exerts a profound influence on the resistance of the block to the other. For instance, the impregnation of the blocks above the melting zone by slag and iron oxide, though not sufficient to cause them to melt off, accelerates the mechanical and physical losses by making them brittle and very sensitive to temperature changes. Conversely, the continued erosion at this same point constantly exposes a fresh surface to the slag attack. The rupture of the mortar joints from physical causes allows slag to attack the block on greatly increased surface area and often allows the blast to escape through them carrying slag, grit, dust, etc.

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[1] Presented at the Annual Meeting of the American Ceramic Society, Columbus, Ohio, February, 1925. (Refractories Division.)

To place before this body the effect of variations in practice on the life of the blocks a brief statement of the operations involved is in order. Starting from the shell of riveted or welded steel plate with openings for the charging door, tuyères, slag hole and tap hole, and the tuyères in place of the size number, and disposition specified by the builder, the lining of blocks is put in. Angle irons are usually provided beginning two or three feet above the tuyères and at intervals of about three feet to the charging door. Blocks are laid from the mantel to just above the charging door unless iron blocks are used at the latter point, when a belt of the latter about three feet in width is put on top of the refractories. These are very valuable in long heats when most of the charging is done after the cupola is filled. The utmost care is taken in the lining of the hearth and from the top of the tuyères on up to see that the brick lie in immediate juxtaposition with as little grout as possible, the brick being chipped out for angle irons, buckles in the shell, and anything that tends to interfere with the "brick to brick" ideal. Courses are staggered so that vertical joints do not coincide.

The lining being in, it is painted with a thin wash of fire clay and dried thoroughly without forced draft. The shell should become too hot to touch before this firing is finished. The bottom is dropped, the surface allowed to cool, another application of thin mortar made to the surface of the blocks, and the furnace is then prepared for the heat. The doors are put up, bottom rammed in, and enough wood put in to insure the ignition of the coke. Approximately two-thirds of the bed coke is now thrown in and the torch applied. When the wood is all consumed and the coke shows red all around the edges and at all the tuyères the bed is brought to the proper height with such of the remaining coke as is necessary, using a measuring rod to insure accuracy. (The modifications for oil or gas lighting are obvious.) The tuyères are now closed, the breast put in and the furnace is ready for charging. Steel, if used, pig and scrap, in the order named, are dropped carefully into the furnace, taking every precaution to avoid striking the walls with any of the heavy pieces, and at the same time giving the charge as good distribution as possible. A charge of coke is now put in evenly, followed by the stone, and successive charges of iron, coke and stone follow with more and more emphasis being placed on distribution and less and less on possible damage to the lining as the stock line approaches the charging door. When this point is reached the furnace is ready for the blast.

The blast enters through the tuyères and, passing through the ignited coke, burns it to carbon dioxide with evolution of heat the reaction being chemically expressed as:

(1) $$C + O_2 = CO_2$$

The dioxide passing over the heated coke reacts with it to form monoxide:

(2) $$C + CO_2 = CO$$

This reaction, being endothermic, tends to cool the blast, the maximum of dioxide and the minimum of monoxide and oxygen occurring at a roughly conical surface usually some twelve to twenty-four inches from the tuyères—the distance depending on the velocity of the blast and the reactivity of the coke. The "melting zone" of the cupola may be described as the region beginning where reaction (1) has raised the temperature above the melting point of the iron and ending where the reaction (2) has reduced the temperature below that point. There is of course a great amount of heat absorbed by the iron in melting, but the fact remains that there is still a distinct melting zone even in the absence of iron.[1] Ordinarily this zone is about four inches deep and the greatest destruction of the refractories occurs at the point where it intersects the lining.

The first action of the blast, then, is to burn away enough coke to allow the metal of the first charge to come down into the melting zone, it having been preheated by the passage of the hot gases around it. It is there melted and trickles down through the coke to the hearth whence it is drawn off as required. The ash of the coke, the sand of the pig, and the stone combine to form slag, which follows the iron down and is drawn off from time to time as it accumulates, or is sometimes allowed to run out on top of the iron, whence it is removed in various ways not interesting here. By the time the charge is melted another charge of coke drops into place and the process goes on. It is evidently necessary to have enough coke in the charge to fill the melting zone completely and it is equally necessary not to have more iron in the charge than the coke in the melting zone is able to melt, otherwise the bed coke would be used up, the iron allowed to come down to the lower temperature, higher oxygen region—the iron burned, the refractories damaged, and if the bed is not quickly replenished melting stops and the bottom must be dropped—in fact the writer has had several experiences where dynamite had to be used to get the mass out of the stack after such an occurrence.

When the required amount of iron has been put in, charging is stopped and the cupola blown out. This is a trying time for the refractories for there is no fresh cold stock going in to absorb heat and filter the drops of slag and iron out of the blast. Inspection at this time will show a veritable shower of these and particles of white hot coke shooting up first around the edges and gradually from the whole bed, many of them sticking to the brickwork. The particles of iron stuck to the wall burn as soon as the air strikes them, leaving a spot of iron oxide to cause damage on the next heat. When melting is done, the doors are dropped, the refuse removed and the furnace is cooled.

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[1] Belden, U. S. Bur. Mines, *Bull.* **54.**

It is then prepared for the next heat by chipping out all the slag, coke and iron adhering to the walls, especially around the tuyères where it is chilled by the cold incoming blast. The melting zone is then repaired by "daubing" it with a wet mixture of clay and sand, using brick or even blocks if it is deeply attacked. The daubing should practically restore the straight line of the original brickwork but should not be allowed to encroach on the shaft area. The operations as outlined above are now repeated except that the wood and coke should be put in with due regard to the preservation of the daubing and that the first coke should be allowed to get quite hot so as to dry the daubing thoroughly before charging is begun. The first charge especially should be put in meticulously, for if any considerable amount of mud is knocked off of the wall the blocks are left exposed, and the tuyère below is very likely to be bunged up for the heat.

A general inspection of the brief summary above shows that we have three principal factors to consider: the lining, its chemical character and its physical condition; the stock, its chemical character and physical condition; and the blast, its velocity and temperature.

The Lining

It is not the purpose of this paper to discuss the properties of the blocks themselves. It is assumed that they are true to shape and free from visible defects which is generally true of the products of reliable makers. That they should be kept out of the weather is possibly not as generally known as it should be, for serious deterioration occurs upon exposure, especially if subjected to alternate freezing and thawing.

Probably the most important item in the lining of the cupola is the clay used as a grout. Unless this is as refractory as the blocks, it melts away leaving them exposed to the destructive influences and may even dissolve some of the blocks in melting. This point is stressed particularly by Dr. Moldenke (P. I. F.) who states that unusually poor results with linings are invariably traced to the use of local clays of low melting point.

The integrity of the lining is of fundamental importance and calls for the highest skill of the brick mason. Each block should lie snugly against its neighbors with the least possible amount of filling and should fit closely to the shell. Defects in the shell often cause considerable trouble in this respect—buckles, rivets and even the desirable angle irons contributing in no small degree to the failure of the blocks. Welded shells offer quite an advantage in this regard, as the troublesome rivet is entirely eliminated, which, even though countersunk, persists in working loose under the continual vibration, contraction and expansion and allows the blast to escape through any channels that may have opened up through the refractories.

It is safe to say that daubing the melting zone is the real *bête noire* of the cupola tender. Here we have a ring around the cupola melted out of blocks which are the utmost effort of the experienced and well equipped manufacturer, placed in position by a highly skilled artisan working under the most favorable conditions. The tender now has some clay and sand, a mud box and a plasterer's hoe, a hose or perhaps a bucket of water, and a half hour's time with which to repair the lining for another heat. The curious thing about it is not that he so frequently fails but that he ever succeeds. His mud must be wet enough to work easily, but if too wet it will crack and perhaps blow off when heated. It must be sticky enough to adhere to the glazed surface of the blocks, open enough to dry without cracking, and refractory enough to withstand the high temperature of the furnace. There are probably as many different daubing mixtures used as there are cupola tenders. In many small foundries a smear of strong molding sand is all that is attempted, but in long heats the mixture of clay and fire sand described by Dr. Moldenke (P. I. F., p. 380) is almost universal, the percentages naturally depending on the fatness of the clay. The mixture used by the writer for many years was one-fourth each of a very fat yellow clay, a rather lean fire clay, silica sand and crushed fire brick. This batch had excellent properties except for its melting point, which was low on account of the highly ferruginous yellow clay. Recently, there has been available a very fat, highly refractory fire clay which has eliminated the other two clays—the mixture now being one-third each fire clay, sand and crushed fire brick prepared as before in a mill. The improvement in the appearance of the furnaces at the end of the heat has been most remarkable since this new clay came to hand. In long heats where the cutting under the best conditions runs as much as three or four inches, the daubing should be used simply as a seating for brick placed flatwise in the ring. Splits are very useful for this purpose and should always be kept on hand. Mica schist is very convenient and satisfactory, though it is not at all porous and the lining must be heated carefully if large pieces are used to prevent the steam blowing them off.

An important factor is the time allowed by the working conditions of the foundry for getting the furnace ready for the next heat. In plants using short melts this is of little concern, but where a cupola is run all day and must be ready for charging early the next morning the temptation is strong to bring the cupola men out as late as possible and rush the work. This usually results in a very poor job—the chipping is not thoroughly done, the daubing is not carefully put in, the wind is turned on to hasten the lighting off, and the charging is done helter-skelter. It is far better to have the furnace put up at night on a separate shift—then everybody has time to do the job well. Often this requires cooling off the walls with a hose so that the men can work in the shaft, which sounds like bad treatment and probably does injure the lining, but good blocks stand it remarkably well. Curiously enough the blocks seem to give better service when the furnace is run every day, even though cooled with water, than when run every other day and consequently allowed to cool naturally. The writer has three distinct conditions to handle, a description of which is interesting in this connection. First are the large pipe foundry cupolas, two running every day and two every night. The heats are about ten hours in blast, melting fifteen tons per hour. For the day shift they are lighted off at 11.00 P.M., charging begins at 2.00 A.M. and the wind goes on at 3.30 A.M. Bottom is dropped about 1.30 P.M. and water turned onto the dump immediately. By 5.00 or 6.00 P.M. the refuse has been removed and the men are chipping out, copious streams of water being used to cool the stack to the point of tolerance. By 9.00 or 10.00 P.M. the daubing is in and the furnace is ready for another cycle. The night furnaces are on the same basis, placing A.M. for P.M. In the special foundry there are two cupolas which run on alternate days, the shifts being about eight or nine hours and no water cooling is necessary. In the specialty shop, one cupola is run every day, but as the heats are only about two hours, it has ample opportunity to cool off before the tender has to go into it. The following figures tell the story:

Cupolas	Cooling	Life of lining	No. hours heat per lining
Pipe Foundry	Artificial	Six Months	1500
Special Foundry	Natural	Twelve Months	1300
Specialty Shop	Natural	Twelve Months	600

The only explanation of this that occurs to the writer is that the pipe foundry cupolas never really get cold except over Sunday and they consequently do not suffer as much contraction between heats. The reason for the poor showing of the specialty cupola is that so much of its heat is blowing out which, as explained above, is particularly hard on the lining. The special foundry operates on higher temperatures than the others, which may explain the slight difference there, but it would not seem to make up for the water treatment.

The Stock

The cupola charge consists of fuel, flux and metal in the general proportions of about 12 fuel and 2 flux to 100 parts of metal. The properties of any one may greatly affect the proportions above and the temperature requirements of the foundry are the prime consideration in fixing the coke, but the general average will not be far from that given.

Fuel

Practically the only fuel now used is coke. Formerly, only beehive coke was considered for foundry work but the by-product oven is fast winning its way. There is not much difference between them in the final analysis, for though the beehive is not so readily dissolved (Eq. 2, p. 722), the chances for oxidation are greater. Further, the angular structure of the beehive is against it as is also the fact that the by-product coke is commonly better sized. The effect of one of those huge blocks of strong angular beehive coke sometimes seen charged, with several hundred pounds of iron holding it against the wall in its descent, can readily be imagined. On the other hand there is more chance of getting a lot of "breeze" in the by-product than the beehive. A very hard coke is unduly abrasive and a very soft coke crushes under the burden, so neither extreme is desirable. The relation between structure and combustibility or reactivity has not yet been satisfactorily determined, but in general these properties would seem to diminish as the hardness increases. Therefore, a soft soluble coke would demand a higher fuel consumption than a hard insoluble one with consequently more ash. It might well be that the hard coke, being less reactive than the soft coke, would save the lining more by reducing the slag than the soft coke would by lower abrasion. The reaction (Eq. 2) of carbon and carbon dioxide to the monoxide is a function of the time of contact which depends on the surface exposed, therefore, the smaller the coke the greater the amount lost as monoxide. Small coke should be avoided for this reason as well as for its tendency to pack. The author's experience is that coke of 3 to 5 inches is the most satisfactory and that extreme hardness is neither necessary nor desirable.

The amount and composition of the ash is by far the most important characteristic of the coke, though as explained above, the percentage of ash is not the ultimate consideration, for a coke with 10% ash which allows a melting ratio of 10 to 1 will be better than one with only 9% ash which will permit a ratio of only 8 to 1. The writer is not familiar with any analytical work on the ash contents of the various cokes, but it is apparent that the more iron it contains the greater will be the damage, and that the higher the silica present the more flux will be needed to take care of it with consequently more slag to act on the lining. Assuming that there is no difference in the composition of the different ashes and that the efficiency of the fixed carbon is the same, the flux will increase more rapidly than the ash for each increment of ash demands an equivalent of flux, which requires more coke for melting it, which brings in more ash to be fluxed, etc.

The writer once tried a very fine looking coke with excellent physical properties, but 17% ash. In an experimental cupola on short runs where slagging was not necessary it gave excellent results, but in the regular operation, where it was necessary to slag, the amount of flux required was so great that it was impossible to melt hot enough for the work with a ratio of only 6 to 1, although the usual ratio with the standard 10% ash coke was about 9 to 1 for this particular foundry. The cutting out of the lining on this heat was terrific. To be sure there was not some other cause of the trouble, the experiment was repeated but the results were identical, though the blast was manipulated through a wide range in the effort to get the iron hot.

Flux

The principal flux in use is limestone though other forms of calcium carbonate, such as oyster shells and marble waste, are used where local conditions are favorable—these latter being particularly desirable on account of their purity. Fluorspar is used sparingly in some cases and is a very quick and valuable means of thinning the slag when it is "sticky" but should be used only as medicine for it is very destructive to the lining.

The role of magnesium is not quite clear. Dr. Moldenke says it is "an excellent fluxing material" and Johnson ("Principles, Operation and Products of the Blast Furnace") cites an instance of very fine results from its use in a blast furnace making basic pig iron. Field, however (Bureau of Mines, Technical Paper 157), shows a pronounced increase in the viscosity of a synthetic slag by substituting 20% MgO for 20% CaO. Field and Royster in a later paper (Bureau of Mines, Technical Paper 187) show the lowest viscosity of actual blast furnace slag at 5.5% MgO, the limits investigated being 1.5 to 7.5%. Their conclusion is that "the difference between the two is not caused by the magnesia as such, but by the fact that its presence lowers the percentage of lime relative to alumina and silica. In other words, magnesia and other minor constituents, if present in amounts not exceeding 14%, act as more or less neutral substances and can be left out of consideration." The writer has used limestones varying in magnesia from 1% to 12%, but has never been able to detect any particular effect traceable to this variation. Iron is objectionable but is usually present in very small percentages and is lost in the shuffle.

The most important point to be watched in the flux is the amount of insoluble residue, which is mostly clay and silica. As one pound of sand or clay requires nearly three pounds of calcium carbonate to produce a fluid slag, each per cent of such impurity lessens the amount of available flux by four, this additional slag requires more coke to melt it which adds more ash to be fluxed, etc., *ad nauseam*.

Metal

Probably the most desirable charge that can be imagined is one consisting of iron balls two or three inches in diameter and free from sand and rust. Such a charge would allow of perfect distribution in the cupola, would give a minimum resistance to the blast, would require only sufficient flux for the ash of the coke, would absorb heat rapidly enough for good melting, and would offer very little surface for oxidation. Such an ideal is of course unattainable, but the effect of the actual condition of any given charge may well be measured by its deviation from such a standard. Thus large and unwieldly pieces, such as sows, rolls of various kinds, and all manner of heavy machinery parts are difficult to place properly in the cupola and are slow to absorb heat. The writer once had some steel balls of about 400 lbs. weight to melt. The first one tried was put in without any special precaution and although the heat lasted some two hours after it was charged, it was found in the drop having lost only about half its weight. After that it was found that by putting some half its weight of extra coke just beneath one we could get it melted very nicely. Even where the section is not heavy, a large piece such as a plate cuts down the area available for the blast, and thus increases its velocity while at the same time depriving the stock above it of the contact with the hot gases necessary for preheating. Large hollow articles such as stoves, pipe, acid eggs and the like, when charged unbroken, not only divert the blast but, when they do finally melt, cause a sudden rearrangement of the whole body of stock above them with consequent danger of disturbing the orderly arrangement of the charges. Long pieces such as rails and arbors often get cocked up against the wall and cause trouble from scaffolding.

Fine scrap such as borings, shot and sweepings have a tendency to run down ahead of their turn through the melting zone and into the high oxygen region near the tuyères where they burn and add more to the slag than to the iron. Where they are already rusted, as they usually are, the trouble is increased. Thin stuff such as stove plate suffers from oxidation, 80% being very good recovery in the ladle—the rest going to iron oxide which is, as before stated, the most damaging constituent of the slag. Light steel scrap is even worse for it has not the carbon of the stove plate to protect it. The writer once ran a heat of 5000 lbs. of tin cans, barrel hoops and hack saw blades, from which he obtained 1800 lbs. of the "wildest" metal he ever witnessed—a recovery of 36%.

Pig iron is cast in three ways: in sand molds, in iron molds laid out as the sand molds with sand runners leading to them, and in the chill molds of a casting machine. The sand cast is covered with sand, but usually of nice size. The chill cast is fairly clean but often the pigs are too large and heavy. The machine cast is free from sand but is often made too heavy, especially for small cupolas. The effect of sand on the pig is of course the same as it is in the coke or stone except that in addition to the increase of flux required it makes the pig more abrasive. It remains then to examine these forms of pig iron from the chemical point of view. The combined carbon is lowest in the sand cast and highest in the machine cast on account of the more rapid cooling of the iron in the latter case. The combined carbon is what determines the melting point and the total carbon determines the freezing point. As an illustration, consider two pure iron-carbon alloys of 4.3% carbon, one of which has been cooled so slowly that all its carbon is free, or graphitic, and the other cooled so quickly that all its carbon is combined. We have in the first case a mixture of pure iron whose melting point is 1535°C with carbon mechanically enmeshed sufficient to lower its freezing point to 1135°C. In the second case the melting point is 1135°C which is also its freezing point. Of course it is impossible to melt quickly enough to prevent some solution of the graphite by the dead soft matrix of the gray iron but with the large thick flakes of graphite and the large grains of ferrite usually present in the soft irons, the action is probably quite slow until very high temperatures are reached, so that in the case mentioned we might well expect a combined carbon of only 1% or 2% by the time it begins to melt which would, even in the latter case, give us a melting point of about 1350°, or over 200° higher than that of the white iron. Dr. Moldenke (P. I. F., pp. 204) cites an actual test where a difference of 3% combined carbon gave a difference of 120° in the melting point in favor of the gray iron. The influence on the lining comes from the necessity of maintaining the bed of coke at a greater height for the chilled iron so that it will acquire the necessary super-heat for casting after it is melted, whereas the gray iron possesses it as soon as it becomes molten. "Off-grade" irons, which are usually produced

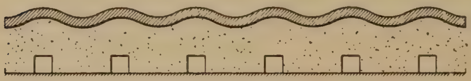
TABLE I

	Per cent scrap										
	20	25	30	35	40	45	50	60	70	80	90
	150	100	110	65	65	80	150	125	110	35	75
	150	200			50	40	110	40	125	40	115
	175	100			60	80	110	70	75	35	75
	150	180			70	130	80		15	65	45
	130	160			75		110		50	35	30
	175	125			75				60	60	100
	50	100			160				75	45	
	160	110			135				75		
	125	200			75				50		
	135	150									
	140	160									
	185	135									
	150	125									
		130									
Ave.	144	141	110	65	85	82	112	78	65	45	73

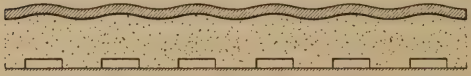
Av. % scrap	Heats
20–30	141
35–50	92
60–70	70
80–90	58

when the blast furnace is in trouble, commonly contain dissolved oxides which are not only destructive to the lining but very troublesome in the foundry. They should never make up a large proportion of the charge if good castings are desired.

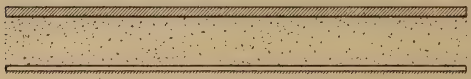
Much has already been said about scrap, but from the present point of view the writer feels that it is the most important feature of the charge. As stated before, oxidation is undoubtedly the chief cause of its destructiveness especially when using light scrap such as stove plate and "country" steel. The writer used for several months a charge of 50% light to medium steel scrap, 25% stove plate, and 25% agricultural scrap and foundry returns. This was for duplexing in a basic electric furnace and was not required to be very hot, but the volume of slag was enormous, the coke ratio had to be kept at 7 to 1, and the melting zone seldom went ten hours without showing a hot spot. To check up the influence of scrap on the lining the records of the company were carefully gone over and Table I was prepared. These records were only begun in the latter part of 1917, but the period since then includes the very interesting experience of the electric furnace which allowed the use of the high percentages of scrap indicated. The table gives the number of heats per lining listed under the scrap percentage used during its life. There are, of course, inconsistencies but the general trend is striking. Most of the extraordinarily good results on the high scrap mixtures were obtained by relining the melting zone with new blocks. This was not entered in the records as a "lining." With low scrap mixtures this is never done as the abrasion in the stack is what determines the life in this case.



(A) Square Tuyeres occupying 25 per cent of Perimeter



(B) Rectangular Tuyeres occupying 50 per cent of Perimeter



(C) Flat Continuous Tuyere

Tuyere area same in all cases.
Melting zone 18" above tuyeres and 4" wide.

FIG. 1.

Blast

The chief factors to be considered are velocity, temperature and the persistence of oxygen. A great deal in this connection may be attributed to the stock as has already been indicated: large pieces cutting down the area causing a rush of gas through the opening remaining; large coke allowing oxygen to persist throughout the stack (Belden, U. S. Bureau of Mines, Bulletin 54, 14); small coke causing channels; slag being too viscous to run out, thus clogging up the furnace around the tuyères. The fundamental consideration, however, is the size, shape and distribution of the tuyères. The ideal is a flat tuyère occupying the whole circumference of the furnace. This gives a smooth shaped melting zone of the same height on the walls everywhere and easy to start off with the correct bed. Figure 1 shows roughly the intersection of the melting zone with the walls for three types of tuyères: square ($b = d$), rectangular ($b = 2d$), and the flat tuyère ($b = 4d$) now gradually supplanting these two. It is apparent that with either of the first two a level bed will be either too low for just over the tuyères or unnecessarily high for points between them and it would be impossible to put in a bed of such shape. Upper tuyères cause a weakness in the most important courses of the blocks and add oxygen to the blast at a very troublesome point. They serve no useful purpose, for better results can be obtained by using the correct amount of air through one row, if this is of the proper dimensions.

The correct blast pressure depends on the character of the charge, especially the coke, the height of the stack and the diameter of the cupola. It should be sufficient to drive the blast well into the shaft, otherwise there will be an undue amount passing up against the wall and the interior of the stack column will be worse than useless. Table II shows the inside diameters of the cupolas used by the writer and the blast pressure found by experiment to give the best results. The attempt was once made during a period of depression to run the 66-inch stacks on 6 ozs. pressure so as to slow them up, but after several "freeze ups" it was abandoned. One experience stands out in particular. The furnace had run cold for several hours and it was decided to drop it without waiting to blow out. A column of slag, coke and iron of about three feet in diameter was dropped out, that was evidently the first iron charged. It had simply lain in the middle of the cupola and fused enough to sinter it together but there it stayed until the bottom was dropped. Half pigs had melted off and left the other half stuck in the mass.

TABLE II

Inside diameter, inches	Pressure, ounces per sq. in.
66	12–14
60	10–12
54	8–10
42	6– 8
18	3– 4

Far more damage is done to linings and castings by too much blast than by not enough—the natural tendency being to "crowd 'er" and get the heat off as quickly as possible. Chief among high pressure troubles are oxidation of the iron with corresponding increase in the volume and corrosiveness of the slag; bridging or scaffolding at and just over the tuyères from chilled slag and iron; and a tremendous increase in the abrasive effect of particles of sand, slag and coke which are blown up the walls like a sand blast. The effects of oxidation are seen in the shortened life of the molten metal and in honeycombed castings. The slag becomes "foamy," often contains considerable iron shot and solidifies to a porous mass of a dull black or brown color in striking contrast to the dense, vitreous structure of good slag with its glossy, dark green color. Accidental stoppage of part of the tuyère area by a "drop out" of the daubing frequently causes the phenomenon even under the best conditions and, unless the tuyères can be opened up, the destruction of the lining is very severe. In fact, one such off heat will cause more damage to a lining than weeks of normal operation.

Furnaces running on high pressure are particularly liable to bridge. The trouble starts by particles of slag freezing as they trickle through the cold blast catching coke and iron to form a dense mass that obstructs the wind and gives it increased velocity through the remaining space. The effect is cumulative and may even go to complete stoppage of the blast. A poor daubing material will often cause trouble by melting off early in the heat and freezing over the tuyères and the same may be said of cheap brick used for patching or lining. Not the least trouble from a bridge is the damage to the lining caused by removing it. Frequently sledge hammers are necessary for this work and the brickwork is severely jarred with consequent danger of cracks.

Little can be said of the blast temperature as it is obviously dependent on the proportion of iron to coke and on the character of the coke. With a very pure, highly reactive coke good nine-inch blocks can easily be melted through in a few hours as the writer has personally seen when using pitch coke in excess. Iron was actually tapped at 1600°C in one experiment with this coke which would probably mean at least 1800°C somewhere in the cupola, if not more. No refractory could be expected to stand such temperatures under the conditions of actual operation. Where excessive temperatures are required for the work, the life of the linings will inevitably be short, but linings are cheaper than rejected castings.

In conclusion, it may be said that in one point only does good foundry practice work against the lining and that is high temperature. As the normal working of the cupola gives hot iron, cold iron is a sure sign that something is wrong. It is far better to melt hot and cool with scrap than to court disaster by melting cold. Really, in the last analysis, it is doubtful whether correct melting will attack the lining any faster than cold melting on account of the increased chances of oxidation in the latter. In all other respects the interests of the foundry and of the liner are identical. The remarks given in this paper concerning methods of lining, daubing, lighting and charging; the remarks about tuyères and blast pressure; and the remarks about fuel, flux and the character of metal would apply just as well in a paper on foundry practice as they do here. Iron oxide has been discussed at length, as to its effect on the linings, but its effect in the foundry is much more important and costly. It would not be too much to say that the finest thing that could be done would be the elimination of oxidation in the cupola, the price of which is vigilant application of the fundamental principles and painstaking attention to the humdrum of every-day routine.

METALLURGIST, AMERICAN CAST IRON PIPE CO.
BIRMINGHAM, ALA.

Discussion

G. A. **BOLE**: We should know more accurately the service conditions that exist in a cupola in order to be able to prescribe more surely a refractory for the various areas. Some years ago the Bureau of Mines attempted studies of the temperature distribution and the atmosphere in the cupola. They had a great deal of trouble, however, in getting data, especially on the temperature due principally to the descending charger. They placed thermocouples at various depths in the charge and at various heights above the tuyères. They also took gas samples at the same places. This work is reported by A. W. Belden.[1]

W. G. **GRIFFITH**: We find that one very large foundry in the country wishes a brick as dense as it can possibly be made and they are able to get reasonable refractory values from that sort of brick.

There is another foundry that consumes an immense amount of material that insists on a blast furnace quality brick throughout and they will listen to nothing else.

That is obviously a grave mistake and a little getting together on this point would result in better foundry refractory material. As it is well known, the refractory manufacturer is usually limited in his choice of raw materials to plastic and flint clay. To secure the greatest refractory value from his material enjoins the use of the greatest quantity of flint clay consistent with the necessary strength in structure of the material which he is producing. This is so because ordinarily the plastic clays have a considerably lower refractory value than the flints. If the manufacturer is confronted with a situation where he is required to produce material to resist high heats and at the same time provide an extremely tough material, he ordinarily meets the emergency by reducing the more refractory raw material and strengthening the structure with the plastic, or less refractory material. He goes as far in this direction as he thinks it is safe, and tries to make the adjustment with as little sacrifice as possible in either direction, that is, toward the reduction of the refractory value and the sacrifice of density. It is very plain that if the manufacturer was not required to combine two inharmonious qualities in the same brick, he could meet the situation much better.

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[1] U. S. Bur. Mines, *Bull.* **54.**

If he were allowed to make a hot zone brick of his best material, having in mind only the conditions that obtained in this zone, and if on the other hand, he were permitted to make an extremely dense brick from his plastic clay to meet the conditions which obtain higher up in the cupola and if these two different materials, each suited to its own place, were used, I believe that a great deal of this complaint would be obviated. I fully realize that carrying two stocks of material, and the possibility of confusion would be an inconvenience, but as it is made plain by this discussion that a serious problem exists, I believe that this inconvenience is the proper burden of the consumer, and, until he has made this proper effort he should not lay all of his woes on the back of the manufacturer. The manufacturer will be glad to work with the consumer and will take an interest and pride in the production of better cupola linings if he can secure the coöperation of his customer. Of course, this coöperation is sometimes secured, but from my experience, it is not general by any means.

L. C. HEWITT: There are a number of conditions that seem to affect the life of cupola blocks, such factors as: size of cupola, rate of melting in proportion to size, that is, pounds per square inch of area per hour, time taken for total melt, total tons melted, makeup of charge whether iron or steel, fluxes used and quantity, height of coke beds, quality of coke, ratio of coke to iron, blast pressure and tuyère ratio to cupola area.

In this case, of course, we are comparing in a sense one cupola against another, whereas, Mr. MacKenzie's paper, I believe, deals particularly with the conditions that might affect the refractory life in any one cupola.

EFFECTS OF COMPOSITION ON THE PROPERTIES OF SHEET STEEL ENAMELS[1]

By H. G. Wolfram and W. N. Harrison

ABSTRACT

The effects produced by the substitution of feldspar for flint and flint for feldspar together with variations in other constituents commonly used in enamels were studied with reference to their resistance to mechanical shock, thermal shock and acid attack. Tests were made on three series of enamels of twenty each which were applied to 8-inch steel dinner plates over a standard ground coat. The enamels of the series containing both flint and feldspar were found to be most satisfactory for general use. Results indicate that enamels having certain excellent properties, making them more suitable for special purposes, may be found in the other two series.

Introduction

Investigations of the properties of enamels for sheet steel as affected by changes in composition have been largely confined to (1) methods of testing, (2) the cause and remedy of some particular defect, or (3) the effects of substituting some one ingredient for another. Manufacturers, anxious to apply the results obtained, are handicapped by the relatively small number of available enamels of satisfactory properties. The need for more information was considered sufficiently urgent by the Bureau of Standards to justify determination (1) of the effects produced by greater changes in composition than have heretofore been attempted and (2) whether the present limited number of enamels could be increased.

Plan of Investigation

Three series of enamels were studied. Series I, in which the refractory[2] portion consisted entirely of feldspar, represents one extreme. Some manufacturers substitute feldspar for flint to increase the coefficient of expansion to equal nearly that of the metal bases without materially altering the refractoriness of the enamel. Series II presents more closely the commercial enamel containing feldspar and flint in the ratio of 7:5. Series III, the other extreme, has flint only as the refractory portion. This, of course, should produce a decrease in coefficient of expansion. Because the composition of commercial feldspars varies whereas flint is more uniform, replacement of all feldspar by flint might insure more uniform results.

In each series various fluxes and opacifiers were substituted systematically one for another.

The enamels were applied to 8-inch steel dinner plates; tested for resistance to thermal shock and acid attack; examined for relative opacity

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[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce. Recd. Sept. 11, 1925.

[2] See H. F. Staley, Bur. Stand., *Tech. Paper* **142**, pp. 7–28.

TABLE I
BATCH WEIGHTS
(Parts of the whole)

Enamel No.	Feldspar[1] and flint	Borax	Boric acid	Sodium nitrate	Soda ash	Cryolite	Fluorspar	Sodium antimonate	Zinc
1	60	40.9	..	4.8	11.3	10	..	..	..
2	60	40.9	..	4.8	11.3	..	10	..	..
3	60	40.9	..	4.8	11.3	..	..	10	..
4	60	40.9	..	4.8	11.3	..	..	..	10
5	60	20.0	14.8	4.8	..	10	10	..	..
6	60	20.0	14.8	4.8	..	10	..	10	..
7	60	20.0	14.8	4.8	..	10	..	..	10
8	60	20.0	14.8	4.8	..	..	10	10	..
9	60	20.0	14.8	4.8	..	..	10	..	10
10	60	20.0	14.8	4.8	..	..	..	10	10
11	60	13.62	..	4.8	18.8	10	10	..	..
12	60	13.62	..	4.8	18.8	10	..	10	..
13	60	13.62	..	4.8	18.8	10	..	..	10
14	60	13.62	..	4.8	18.8	..	10	10	..
15	60	13.62	..	4.8	18.8	..	10	..	10
16	60	13.62	..	4.8	18.8	..	..	10	10
17	60	13.62	..	4.8	1.72	10	10	10	..
18	60	13.62	..	4.8	1.72	10	10	..	10
19	60	13.62	..	4.8	1.72	10	..	10	10
20	60	13.62	..	4.8	1.72	..	10	10	10

TABLE II
COMPOSITIONS MELTED, CALCULATED CUBICAL EXPANSIVITY AND RESULTS OF TESTS

	Variable Constituents (% of total)						Series I[2]					
							Ratings					
Enamel No.	Boric oxide (B_2O_3)	Sodium oxide (Na_2O)	Cryolite (Na_3AlF_6)	Fluorspar (CaF_2)	Sodium antimonate ($NaSbO_3$)	Zinc oxide (ZnO)	Cubical coeff. expansion ($\times 10^{-7}$)	Thermal test (units)	Acid test (units)	Opacity (units)	Impact on edge (ft.-lbs.)	Impact on center (ft.-lbs.)
1	10	10	10	..	..	..	388	11	19	2	0.245	0.325
2	10	10	..	10	..	..	339	11	15	1	.179	.313
3	10	10	..	..	10	..	360	11	43	9	.183	.275
4	10	10	..	..	..	10	332	2	21	8	.177	.312
5	10	..	10	10	..	..	313	8	36	2	.154	.300
6	10	..	10	..	10	..	334	7	51	4	.145	.338
7	10	..	10	..	..	10	306	3	12	9	.150	.281
8	10	..	..	10	10	..	285	13	27	10	.173	.331
9	10	..	..	10	..	10	257	11	22	5	.192	.306

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[1] Series I contains 60 parts feldspar, no flint.
Series II contains 35 parts feldspar and 25 parts flint.
Series III contains 60 parts flint, no feldspar.

[2] Constant portion 60% feldspar, 5% sodium oxide and 5% boric oxide, no flint.

10	10	..	..	..	10	10	278	15	30	3	.150	.275
11	..	10	10	10	..	..	412	1	31	4	.276	.256
12	..	10	10	..	10	..	433	1	28	1	.176	.310
13	..	10	10	..	..	10	405	1	28	3	.292	.344
14	..	10	..	10	10	..	384	1	35	9	.253	.275
15	..	10	..	10	..	10	356	11	56	1	.181	.300
16	..	10	..	..	10	10	377	15	30	8	.216	.481
17	..	..	10	10	10	..	358	1	49	10	.230	.250
18	..	..	10	10	..	10	330	5	18	3	.232	.335
19	..	..	10	..	10	10	351	13	20	8	.167	.381
20	..	..	..	10	10	10	302	13	23	3	.167	.275

Series II[1]						Series III[2]					
	Ratings						Ratings				
Cubical coeff. expansion (× 10⁻⁷)	Thermal test (units)	Acid test (units)	Opacity (units)	Impact on edge (ft.-lbs.)	Impact on center (ft.-lbs.)	Cubical coeff. expansion (× 10⁻⁷)	Thermal test (units)	Acid test (units)	Opacity (units)	Impact on edge (ft.-lbs.)	Impact on center (ft.-lbs.)
340	6	43	2	0.184	0.362	273	13	60	9	0.188	0.306
291	12	51	1	.161	.337	224	13	60	5	.209	.425
312	12	60	9	.164	.325	245	14	60	5	.202	.406
284	12	42	8	.178	.343	217	15	60	4	.180	.325
265	11	51	2	.161	.387	198	15	60	4	.173	.450
286	11	51	4	.177	.456	220	15	60	5	.169	.400
258	8	42	9	.185	.450	191	14	60	6	.178	.394
237	13	60	10	.198	.475	171	15	60	2	.194	.381
209	14	60	5	.208	.500	143	11	60	1	.172	.387
230	15	60	3	.181	.325	164	15	60	2	.184	.319
364	7	50	4	.255	.337	298	12	60	3	.169	.344
385	1	60	1	.167	.331	319	11	60	4	.184	.356
357	1	51	3	.185	.331	291	13	60	6	.168	.294
336	11	60	9	.161	.325	270	13	60	1	.173	.256
308	7	60	1	.183	.387	242	11	60	5	.177	.376
329	12	54	8	.181	.331	263	14	60	1	.169	.375
310	9	60	10	.175	.356	244	15	60	6	.181	.331
282	11	47	3	.186	.393	216	15	60	4	.191	.400
303	11	45	8	.175	.331	237	15	60	5	.175	.306
254	15	60	3	.166	.387	188	14	60	2	.175	.306

and subjected to impact tests. The results of these tests are correlated with the enamel compositions.

The compositions of the frit, as calculated, consisted in all cases of 60% feldspar, or flint, or both and at least 5% each of boric and sodium oxides.

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[1] Constant portion 35% feldspar, 25% flint, 5% sodium oxide and 5% boric oxide.

[2] Constant portion 60% flint, 5% sodium oxide and 5% boric oxide, no feldspar.

The remaining 30% was made up of equal percentages of three of the following commonly used constituents: boric oxide, sodium oxide, cryolite, fluorspar, sodium antimonate and zinc oxide. All possible combinations of any three of these materials were employed with each of the different refractory portions. This gave a total of 60 enamels. The batch compositions are given in Table I and the compositions of the frits are included in Table II.

Preparation

Small batches of the enamels were first prepared to observe their working properties; after this, batches of approximately 30 pounds each were smelted in a rotary smelting furnace (to simulate more nearly plant conditions) and prepared for application. The enamels were applied over a standard ground coat by dipping, and fired for $1^{1}/_{2}$ to $2^{1}/_{2}$ minutes at 850° to 875°C (1562° to 1607°F) in a gas-fired muffle having a chamber 20 x 48 inches and 8 inches to the spring of the arch. The standard ground coat used was:

GROUND COAT 420

Frit (batch composition)		Frit (computed composition after melting)		Mill batch	
Borax	33.3%	Feldspar	30.90%	Frit	100.0 lbs.
Feldspar	23.8	Clay	4.45	Clay	7.0 lbs.
Flint	21.9	SiO_2	28.40	Borax (Sol.)	1.5 lbs.
Soda nitrate	7.1	Na_2O	10.40	Water	50.0
Potassium nitrate	4.3	K_2O	2.60		
Fluorspar	4.2	B_2O_3	15.84		
Clay	3.9	CaF_2	5.45		
Cobalt oxide	0.4	CO_3O_4	0.52		
Manganese oxide	.7	MnO_2	.84		
Nickel oxide	.4	Ni_2O_3	.60		
	100.0		100.00		

Methods of Test

Thermal Shock Resistance to thermal shock was tested by placing a plate containing 25 cc. of water on a small gas stove of the ordinary star burner type, the height of the flame being controlled by a constant gas pressure. After boiling to dryness, the plate was allowed to remain over the flame for 15 seconds, and then, while still over the flame, 25 cc. of water at room temperature was poured rapidly into it. This procedure was repeated ten consecutive times unless failure resulted sooner. A chip 0.25 inch or more in diameter was considered as indicating a failure and each piece of ware which failed on or before the tenth treatment was given a rating number corresponding to the number of treatments required to produce failure.

It was found upon examining the results of these tests, that ratings could be given to those plates which withstood the ten tests, on the basis of defects not serious enough to be classed as failure. These plates were given ratings from eleven to fifteen, the highest indicating the complete absence of defects. This test is very severe, necessarily so to insure failure of a majority of the pieces within a reasonable number of treatments.

Impact Tests

The impact tests employed in this work are the same as those used by Danielson and Sweely.[1] The apparatus is essentially a pendulum with a hammer of a definite mass (6 oz.). The kinetic energy (in ft.-lbs.) of this hammer at the instant of striking is taken as a measure of the severity of the blow. The kinetic energy of each succeeding blow is increased by equal increments, making the blows progressively more severe, until the test piece fails.

The results are directly comparable only when specimens and apparatus are of the same size, shape and mass and with the same increments of kinetic energy of the hammer blows. The plates were tested for resistance to impact at the center of the bottom and on the curved surface, the outside of the plate being struck by the hammer. In both cases the blow was normal to the surface at the point of impact. In these, as in the thermal tests, a chip 0.25 inch in diameter was considered as indicating a failure. Two hundred and forty plates representing the sixty enamels, were tested at the center and at four equidistant points on the curved surface. The average of the energies required to produce failure in the respective tests represents the rating of each enamel.

Opacity[2]

The relative opacity of the enamels was estimated by visual comparison by two independent observers who examined four sample plates of each enamel in order to minimize the effect of any accidental differences in apparent opacity. The differences in the ratings resulting from the comparisons by the two observers were small. There being a sufficient range of opacity to warrant such a division, the 60 enamels were divided into ten groups of six each and rated from one to ten, the highest number representing the greatest opacity. A good commercial enamel, tested under these same conditions, was rated at seven.

Resistance to Acid

The method used for testing enamels for resistance to acid has been previously described[3] and depends on the action of 1% acetic acid solution on the enamel at room temperature, for ten consecutive, five-minute periods. The plate to be tested was tilted at an angle of about 8° and enough acid solution poured in to cover half the bottom of the plate. After five minutes, the acid was removed, the plate rinsed, dried thoroughly and examined. This test was repeated ten times, and the extent of the attack observed after each acid treatment and rated as follows: 6—no visible effect; 5—very slight loss of gloss; 4—slight loss of gloss; 3—complete loss of gloss; 2—slight etching; and 1—decided etching. The sum of the ratings for each of the ten 5-minute periods was the final rating of the enamel. An enamel having a rating of 60 showed no visible attack upon completion of this series of tests, while one having a rating of 10 was considerably etched.

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[1] R. R. Danielson and B. T. Sweely, "The Relations between Composition and Properties of Enamels for Sheet Steel," *Jour. Amer. Ceram. Soc.*, **6** [10], 1011–29 (1923).

[2] A number of tests of these enamels with the Pfund colorimeter indicated that considerable time would be necessary to develop a satisfactory method of determining opacity with this instrument. It was, therefore, not used to obtain the ratings given in this paper. The instrument is described by A. H. Pfund, "The Colorimetry of Nearly White Surfaces," *J. Franklin Inst.*, **189**, 371 (1920).

[3] "Relations between Composition and Properties of Enamels for Sheet Steel," *loc. cit.*

Results

General

The results of the tests are in Table II. This table also includes the calculated coefficients of cubical expansion, and the compositions of the frit, showing the systematic scheme for the introduction of the variable constituents. This arrangement facilitates a correlation of the results with the compositions of the frit. The coefficients of expansion of the enamels were calculated from the computed composition of the frit according to the values assigned to the various oxides and compounds by Mayer and Havas.[1] No actual coefficients were determined, but the calculated values, although at best only approximate, give important relative data.

In order to simplify the comparison of the rating of an enamel in one test with its rating in another and to make a comparison of the rating of one enamel with that of another in the same test easier, the data in Table II were reduced to a common basis and are presented in Table III. In this table a rating of 10 indicates the highest standing and a rating of 1 the lowest, all the results on the 60 enamels being taken into account. By the aid of this table one or more enamels can be readily selected as the most desirable of the series for a given purpose or use. Such a choice will depend on the qualities desired. For example, in the application of enamels to shaped ware requiring a cover coat on both sides, a low coefficient of expansion may largely be disregarded as a source of warpage,[2] while in the manufacture of flat ware a consideration of the expansivity is extremely important. Similarly enamels for kitchen ware should be resistant to acid and thermal shock while those qualities may largely be sacrificed for better opacity and resistance to mechanical shock in enamels for flat ware. Enamels which are troublesome to smelt or which produce ware of poor appearance must be avoided in any case.

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[1] Mayer and Havas, *Sprechsaal*, **42**, 497; **44**, 188, 207 and 220. (A list of values for the oxides ordinarily used in enamels is given in "Enamels," by R. D. Landrum and published by Harshaw, Fuller & Goodwin Co. A partial list is also given in Bur. Stand., *Tech. Paper* **142.**)

[2] "Factors Affecting the Warpage of Sheet Iron and Steel in Enameling," Danielson, Hartshorn and Harrison, *Jour. Amer. Ceram. Soc.*, **7** [5], 326–40 (1924).

Considering these qualities with reference to Table III, enamel II-9 might well be selected as the most desirable for shaped ware because: (*a*) as a whole, the results of the tests are higher than for any other of the 60 enamels, (*b*) it is not troublesome to smelt, (*c*) its low coefficient of expansion is not liable to cause any considerable warpage in this type of ware. The slight tendency to crawl which is indicated in the table is hardly enough to overbalance the good qualities and it could probably be overcome.

II-6 shows higher expansivity, no tendency to crawl and a better opacity, at the expense of some mechanical strength, acid resistance and ease of smelting, and might be preferred to II-9.

For flatware, enamels II-1, II-13 and I-14 seem promising because:

TABLE III

PHYSICAL PROPERTIES AND NUMERICAL RATINGS

Series I

Enamel No.	Time smelting, min.	Remarks		Cubical coefficient of expansion $\times 10^{-7}$. Calculated	Relative rating in different tests. Best rating is 10				
		Nature of melt	Finished ware		Thermal test	Acid resistance	Opacity	Impact on edge	Impact on center
1	50	Fluid	Fish scale	388	7	2	2	7	4
2	50	Fluid	Fish scale	339	7	2	1	3	3
3	120	Viscous, frothy	Matt	360	7	7	9	3	2
4	90	Viscous, frothy	Matt	332	1	3	8	3	3
5	60	Very viscous	O. K.	313	5	6	2	1	3
6	65	Slightly viscous	O. K.	334	5	9	4	1	4
7	45	Fairly fluid	O. K.	306	2	1	9	1	2
8	75	Slightly viscous	O. K.	285	9	4	10	2	4
9	60	Slightly viscous	Crazed and chipped	257	7	3	5	4	3
10	120	Very frothy, viscous	O. K.	278	10	5	3	1	2
11	50	Fairly fluid	O. K.	412	1	5	4	9	1
12	90	Slightly viscous	O. K.	433	1	4	1	3	3
13	60	Fairly fluid	Crazed	405	1	4	3	10	4
14	60	Fluid	O. K.	384	1	6	9	8	2
15	45	Very fluid	O. K.	356	7	10	1	3	3
16	70	Very frothy, viscous	Matt	377	10	5	8	5	10
17	45	Slightly viscous	O. K.	358	1	8	10	6	1
18	40	Slightly viscous	O. K.	330	3	2	3	6	4
19	60	Fluid	Slight crawl	351	9	3	8	2	6
20	75	Viscous	Poor gloss	302	9	3	3	2	2

TABLE III (*Continued*)

Enamel No.	Time smelting, min.	Remarks		Cubical coefficient of expansion $\times 10^{-7}$. Calculated	Relative rating in different tests. Best rating is 10				
		Nature of melt	Finished ware		Thermal test	Acid resistance	Opacity	Impact on edge	Impact on center
			Series II						
1	45	Fluid	O. K.	340	4	7	9	3	5
2	45	Fluid	O. K.	291	8	9	6	2	4
3	55	Slightly viscous	O. K.	312	8	10	7	2	4
4	45	Fluid	O. K.	284	8	7	8	3	4
5	40	Fluid	O. K.	265	7	9	9	2	6
6	55	Viscous	O. K.	286	7	9	10	3	9
7	45	Fluid	Tendency to crawl	258	5	7	10	3	9
8	75	Very viscous	Some tendency to crawl	237	9	10	6	4	10
9	40	Fluid	Some tendency to crawl	209	9	10	7	5	10
10	50	Fluid	Tendency to crawl	230	10	10	6	3	4
11	45	Fluid	O. K.	364	5	9	2	8	4
12	45	Fluid	O. K.	385	1	10	8	2	4
13	50	Fluid	O. K.	357	1	9	7	3	4
14	55	Fluid	O. K.	336	7	10	8	2	4
15	55	Fluid	O. K.	308	5	10	7	3	6
16	80	Very viscous	Matt	329	8	9	7	3	4
17	60	Viscous	O. K.	310	6	10	10	3	5
18	30	Fluid	O. K.	282	7	8	3	3	6
19	60	Fluid	O. K.	303	7	8	10	3	4
20	60	Viscous	O. K.	254	10	10	7	2	6
			Series III						
1	40	Fluid	O. K.	273	9	10	9	3	3
2	45	Fluid	O. K.	224	9	10	5	5	8
3	65	Fairly fluid	Slight crawling	245	9	10	5	4	7
4	40	Fluid	Slight crawling	217	10	10	4	3	4
5	55	Fairly fluid	Crawling	198	10	10	4	2	9
6	65	Fairly fluid	Slight crawling	220	10	10	5	2	7
7	55	Fairly fluid	Slight crawling	191	9	10	6	3	6
8	90	Refractory, viscous, frothy	Crawling	171	10	10	2	4	6
9	55	Fluid	Bad crawling	143	7	10	1	2	6
10	75	Viscous, refractory	Bad crawling	164	10	10	2	3	3

11	50	Fluid	Fish scale	298	8	10	3	2	4
12	50	Fluid	O. K.	319	7	10	4	3	5
13	45	Fluid	O. K.	291	9	10	6	2	2
14	55	Fluid	Slight fish scale	270	9	10	1	2	1
15	55	Fluid	Slight fish scale	242	7	10	5	3	6
16	55	Fluid	O. K.	263	9	10	1	2	6
17	120	Very refractory, viscous	O. K.	244	10	10	6	3	4
18	90	Very refractory, viscous	O. K.	216	10	10	4	4	7
19	110	Very refractory, viscous	O. K.	237	10	10	5	3	9
20	160	Very refractory, viscous	Crawling	188	9	10	2	3	3

(*a*) their higher expansivities would be less conducive to warpage, (*b*) they are not troublesome to smelt, (*c*) they do not produce visibly defective ware, (*d*) their opacities are good, and (*e*) their mechanical strength, as is evident from their resistance to both types of impact, is reasonably high.

Although, for minimum warpage, it would be desirable to use enamels having expansivities approaching that of sheet metal, the data in Table III indicate that this requirement cannot be filled beyond a moderate degree without sacrifice of other desirable properties.

Expansivity vs. Resistance to Mechanical and Thermal Shock

Certain relations between the expansivities and the resistance of the enamels to thermal and mechanical shock are suggested by the data in Table IV. The values in this table were obtained by arranging the enamels of each series, together with their respective thermal and impact ratings, in the order of decreasing coefficients of expansion, and taking the averages of the ten highest and ten lowest coefficients of expansion and of the corresponding numerical ratings for each test. A comparison of these averages indicates that the resistance to the thermal treatment increased with decreased expansivity

TABLE IV

AVERAGES OF EXPANSIVITY AND RESULTS

Series	Enamels	Average expansivity, cubical ($\times 10^{-7}$)	Average numerical ratings		
			Thermal test	Impact on edge	Impact on center
I	First 10	382	6.6	0.222	0.320
	Second 10	308	8.8	.172	.307
	Average	345	7.7	.197	.313
II	First 10	334	7.7	.183	.342
	Second 10	260	12.2	.180	.405
	Average	297	9.9	.182	.373
III	First 10	268	13.1	.179	.350
	Second 10	193	14.2	.183	.379
	Average	230	13.6	.181	.364

throughout the three series. (See Table IV.) That this should be true is apparent from the following considerations:

1. *Enamel of high coefficient of expansion.*—Consider a plate coated with an enamel of relatively high coefficient of expansion, a cross-section of which is represented graphically in Fig. 1. If the expansivity of the enamel is not quite as great as that of the steel, the enamel will be under slight compression (see $A'A'$, Fig. 1*a*). As heat is applied to the bottom of the plate, the layer (L) of enamel will increase in temperature faster than the steel (S) and the compressive stress will be thereby somewhat increased (see A', Fig. 1*b*). On the top side of the plate, the enamel (U) will increase in temperature more slowly than the steel and the compressive stress already existing there will tend to be relieved (see A', Fig. 1*b*).

After the water has boiled out, and the plate has remained dry over the flame for 15 seconds, the temperature throughout the thickness of the plate will tend to become equalized. When cold water is poured onto the surface, the top layer of enamel cools and contracts very suddenly, and much more rapidly than the steel, as illustrated (see $A'A'$, Fig. 1*c*). The slight compressive stress existing is, therefore, quickly replaced by severe tensile stress and the enamel should soon yield to this treatment by cracking and separating from the metal since its tensile strength is probably very much less than its compressive strength.

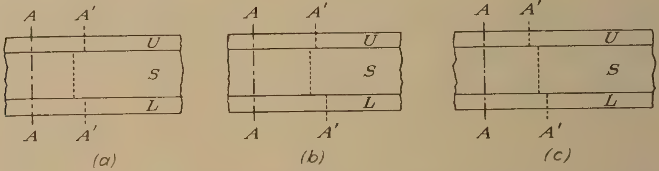

FIG. 1.—Graphical representation of effects produced in enamels of relatively high expansivity, during thermal test. (AA is base or reference line and distance between AA and $A'A'$ represents free lengths, in unstressed state.)

It is reasonable to assume that the strength of an enamel in compression greatly exceeds its strength in tension since enamels are not very different from glasses. Winklemann and Schott[1] in an investigation of 17 different types of glass found that their strength in compression exceeded their strength in tension by 9 to 18 times. Danielson and Sweely[2] found the compressive strengths of eight different enamels ranged between 80,500 and 100,700 pounds per square inch, which compare very favorably with the values for compressive strengths of glasses as found by Winklemann and Schott.

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[1] Winklemann and Schott, "Properties of Glasses," *Ann. d. Phys. und Chem.*, **51**, 697 (1894).

[2] "Relations between Composition and Properties of Enamels for Sheet Steel," *loc. cit.*

2. *Enamel of low coefficient of expansion.*—An enamel having a coefficient of expansion much lower than that of the steel will be under considerable compressive stress (Fig. 2*a*) and as the heat is applied that stress will be increased on the bottom layer of enamel (Fig. 2*b*). Its low expansivity, however, keeps that increase from becoming excessive, and its compressive strength is quite sufficient to withstand the increased stress. The steel, increasing in temperature more rapidly than the top layer of enamel, tends to relieve some of the compressive stress already existing there, but these stresses are partially restored in the 15 seconds of dry heat treatment which follows. As the plate is quenched with cold water, the top layer of enamel cools suddenly and much more rapidly than the steel as in the case of the enamel of high expansivity (Fig. 2*c*), but for two reasons, both due to low expansivity of the enamel, the shock is much less severe. First, the low coefficient of expansion of the enamel tends to keep its rate of contraction down to that of the metal base. Second, if the rate of contraction of the enamel exceeds that of the steel, in spite of the retardation just mentioned, the compressive stress already existing in the enamel must be overcome before any tensile stress can be exerted. Hence, an enamel of low expansivity might stand this test better than one of high expansivity even though the actual tensile strength of the first mentioned were the smaller of the two.

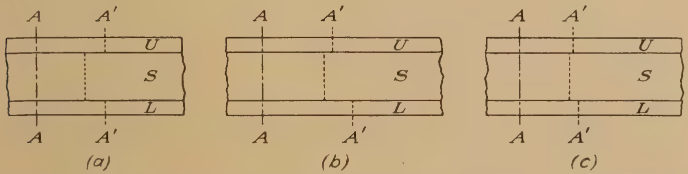

FIG. 2.—Graphical representation of effects produced in enamels of relatively low expansivity, during thermal test. (*AA* is base or reference line and distance between *AA* and *A′A′* represents free lengths, in unstressed state.)

It would appear from this explanation that the ideal condition for resistance to this treatment would require a low coefficient of expansion for the finish coat and a slight increase in expansivity by steps through the first cover and ground coat, all being lower than that of the steel. This is in harmony with the findings of Danielson and Sweely[1] that for high resistance to failure in the thermal test the expansivity of the ground coat should equal or exceed that of the cover.

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[1] "The Relations between Composition and Properties of Enamels," *loc. cit.*

3. Impact test.—That there are certain sources of possible error in the impact tests, and that the actual mechanical strengths of the enamels have effects independent of their expansivities, may account for the fact that the relations between expansivities and resistance to impact are not entirely consistent. Nevertheless, the data in Table IV indicate that resistance to impact on the curved edge of the plate increases with expansivity and vice versa at the center.

That an increase in expansivity should have a different effect for the two different areas subjected to the mechanical shock seems natural when the character of the stresses causing failure is considered. When the blow is on the edge, the curvature of the metal serves as a support and, by tending to lessen the deflection of the surface when struck, prevents excessive tensile stresses from being set up in the enamel opposite the hammer. This rigidity, however, tends to increase the intensity of the force of the blow and, therefore, the layer of enamel next to the hammer is subjected to relatively high compressive stresses. An enamel of low expansivity is already under much greater compressive stress than one of high expansivity and, therefore, less additional stress created by the blow is necessary to cause failure.

In the case of impact on the center, the flat surface is free to deflect, due to the length of span between edges. Compressive stresses are set up in the enamel next to the hammer and over a wide area, due to the deflection of the plate. This deflection, however, causes tensile stresses to be set up on the opposite side of the plate and the fracture occurs on that side in accordance with the assumption that the tensile strength of an enamel is less than its compressive strength. Here low expansivity favors resistance of the enamel to failure because the compressive stress must be overcome before tensile stress can be exerted.

Effects of Ingredients upon Results

The manner in which the results shown in Table II were obtained has already been fully explained. These are rearranged in Table V to show the effects of the variable constituents on the properties of the enamels as indicated by the ratings in the various tests. Since there are six variables and only three are used in each enamel, a comparison may be made by selecting groups of enamels having two of the variable constituents in common and differing from each other only in a single constituent. For example, let us assign arbitrary letters to the various materials used, as follows: *A*, boric oxide, *B*, sodium oxide, *C*, cryolite, *D*, fluorspar, *E*, sodium antimonate and *F*, zinc oxide. The first enamel then would contain in the variable portion *A*, *B* and *C* the second *A*, *B* and *D*; the third, *A*, *B* and *E*; and the fourth, *A*, *B* and *F*. We find that four enamels differ in composition from one another in one constituent only and thus the changes in properties can be compared with

TABLE V
RESULTS WITH CHANGES IN COMPOSITION
Series I

Type	Variables common to type enamel	Thermal Test (A) Boric oxide (B_3O_3)	(B) Sodium oxide (Na_2O)	(C) Cryolite (Na_3AlF_6)	(D) Fluorspar (CaF_2)	(E) Sodium antimonate ($NaSbO_3$)	(F) Zinc oxide (ZnO)
AB	B_2O_3—Na_2O	..	..	11	11	11	2
AC	B_2O_3—Na_3AlF_6	..	11	..	8	7	3
AD	B_2O_3—CaF_2	..	11	8	..	3	11
AE	B_2O_3—$NaSbO_3$	..	11	7	13	..	15
AF	B_2O_3—ZnO	..	2	3	11	15	..
BC	Na_2O—Na_3AlF_6	11	..	..	1	1	1
BD	Na_2O—CaF_2	11	..	1	..	1	11
BE	Na_2O—$NaSbO_3$	11	..	1	1	..	15
BF	Na_2O—ZnO	2	..	1	11	15	..
CD	Na_3AlF_6—CaF_2	8	1	..	..	1	5
CE	Na_3AlF_6—$NaSbO_3$	7	1	..	1	..	13
CF	Na_3AlF_6—ZnO	3	1	..	5	13	..
DE	CaF_2—$NaSbO_3$	13	1	1	..	..	13
DF	CaF_2—ZnO	11	11	5	..	13	..
EF	$NaSbO_3$—ZnO	15	15	13	13	..	..
	Average	9.2	6.5	5.1	7.5	9.0	8.9

Rating
1 Boric oxide
2 Sodium antimonate

3 Zinc oxide
4 Fluorspar

5 Sodium oxide
6 Cryolite

Acid Test (A) B_2O_3	(B) Na_2O	(C) Na_3AlF_6	(D) CaF_2	(E) $NaSbO_2$	(F) ZnO
..	..	19	15	43	21
..	19	..	36	51	12
..	15	36	..	27	22
..	43	51	27	..	30
..	21	12	22	30	..
19	..	..	31	28	28
15	..	31	..	35	56
43	..	28	35	..	30
21	..	28	56	30	..
36	31	..	..	49	18
51	28	..	49	..	20
12	28	..	18	20	..
27	35	49	..	..	23
22	56	18	..	23	..
30	30	20	23	..	..
27.6	30.6	29.2	31.2	33.6	26.0

Rating
1 Sodium antimonate
2 Fluorspar

3 Sodium oxide
4 Cryolite

5 Boric oxide
6 Zinc oxide

Opacity B_2O_3	Na_2O	Na_3AlF_6	CaF_2	$NaSbO_3$	ZnO
..	..	2	1	9	8
..	2	..	2	4	9
..	1	2	..	10	5
..	9	4	10	..	3
..	8	9	5	3	..
2	..	..	4	1	3
1	..	4	..	9	1
9	..	1	9	...	8
8	..	3	1	8	..
2	4	..	..	10	3
4	1	..	10	..	8
9	3	..	3	8	..
10	9	10	..	..	3
5	1	3	..	3	..
3	8	8	3	..	..
5.3	4.6	4.6	4.8	6.5	5.1

Rating
1 Sodium antimonate
2 Boric oxide

3 Zinc oxide
4 Fluorspar

5 Cryolite
6 Sodium oxide

TABLE V (*continued*)

Impact on Edge						Impact on Center					
B_2O_3	Na_2O	Na_3AlF_6	CaF_2	$NaSbO_3$	ZnO	B_2O_3	Na_2O	Na_3AlF_6	CaF_2	$NaSbO_3$	ZnO
..	..	0.245	0.179	0.183	0.177	..	..	0.325	0.313	0.275	0.312
..	0.245	..	.154	.145	.150	..	0.325	..	.300	.338	.281
..	.179	.154	..	.173	.192	..	.313	.300	..	.331	.306
..	.183	.145	.173	..	.150	..	.275	.338	.331	..	.275
..	.177	.150	.192	.150	..	..	.312	.281	.306	.275	..
0.245	..	..	.276	.176	.292	0.325	..	..	.256	.310	.344
.179	..	.276	..	.253	.181	.313	..	.256	..	.275	.300
.183	..	.176	.253	..	.216	.275	..	.310	.275	..	.481
.177	..	.292	.181	.216	..	.312	..	.344	.300	.481	..
.154	.276	..	..	.230	.232	.300	.256	..	..	.250	.335
.145	.176	..	.230	..	.167	.338	.310	..	.250	..	.381
.150	.292	..	.232	.167	..	.281	.344	..	.335	.381	..
.173	.253	.230	..	..	.167	.331	.275	.250	..	..	.275
.192	.181	.232	..	.167	..	.306	.300	.325	..	.275	..
.150	.216	.167	.167	..	..	.275	.481	.381	.275	..	..
.175	.218	.207	.204	.186	.192	.306	.319	.312	.294	.319	.329

	Rating		Rating
1	Sodium oxide	1	Zinc oxide
2	Cryolite	2	Sodium antimonate
3	Fluorspar	3	Sodium oxide
4	Zinc oxide	4	Cryolite
5	Sodium antimonate	5	Boric oxide
6	Boric oxide	6	Fluorspar

Average for the Series (all tests)

1 Sodium antimonate
2 Zinc oxide
3 Sodium oxide
4 Boric oxide
5 Fluorspar
6 Cryolite

RESULTS WITH CHANGES IN COMPOSITION

Series II

		Thermal Test					
Type	Variables common to type enamel	(*A*) Boric oxide (B_2O_3)	(*B*) Sodium oxide (Na_2O)	(*C*) Cryolite (Na_3AlF_6)	(*D*) Fluorspar (CaF_2)	(*E*) Sodium antimonate ($NaSbO_3$)	(*F*) Zinc oxide (ZnO)
AB	B_2O_3—Na_2O	..	..	6	12	12	12
AC	B_2O_3—Na_3AlF_6	..	6	..	11	11	8
AD	B_2O_3—CaF_2	..	12	11	..	13	12
AE	B_2O_3—$NaSbO_3$	..	12	11	13	..	15
AF	B_2O_3—ZnO	..	12	8	14	15	..
BC	Na_2O—Na_3AlF_6	6	..	..	7	1	1
BD	Na_2O—CaF_2	12	..	7	..	11	7
BE	Na_2O—$NaSbO_3$	12	..	1	11	..	12
BF	Na_2O—ZnO	12	..	1	7	12	..
CD	Na_3AlF_6—CaF_2	11	7	..	..	9	11
CE	Na_3AlF_6—$NaSbO_3$	11	1	..	9	..	11
CF	Na_3AlF_6—ZnO	8	1	..	11	11	..
DE	CaF_2—$NaSbO_3$	13	11	9	..	..	15
DF	CaF_2—ZnO	14	7	11	..	15	..
EF	$NaSbO_3$—ZnO	15	12	11	15	..	..
	Average	19.4	8.1	7.6	11	11	10.4

Rating

1 Boric oxide
2 Sodium antimonate

3 Fluorspar
4 Zinc oxide

5 Sodium oxide
6 Cryolite

Acid Test

(*A*) B_2O_3	(*B*) Na_2O	(*C*) Na_3AlF_6	(*D*) CaF_2	(*E*) $NaSbO_3$	(*F*) ZnO
..	..	43	51	60	42
..	43	..	51	51	42
..	51	51	..	60	60
..	60	51	60	..	60
..	42	42	60	60	..
43	..	..	50	60	51
51	..	50	..	60	60
60	..	60	60	..	54
42	..	51	60	54	..
51	50	..	..	60	47
51	60	..	60	..	45
42	51	..	47	45	..
60	60	60	..	..	60
60	60	47	..	60	..
60	54	45	60	..	..
52	53	50	56	57	52

Rating

1 Sodium antimonate
2 Fluorspar

3 Sodium oxide
4 Zinc oxide

5 Boric oxide
6 Cryolite

Opacity

B_2O_3	Na_2O	Na_3AlF_6	CaF_2	$NaSbO_3$	ZnO
..	..	9	6	7	8
..	9	..	9	10	10
..	6	9	..	6	7
..	7	10	6	..	6
..	8	10	7	6	..
9	..	..	2	8	7
6	..	2	..	8	7
7	..	8	8	..	7
8	..	7	7	7	..
9	2	..	..	10	3
10	8	..	10	..	10
10	7	..	3	10	..
6	8	10	..	..	7
7	7	3	..	7	..
6	7	10	7	..	..
7.8	6.9	7.8	6.5	7.9	7.2

Rating

1 Sodium antimonate
2 Cryolite

3 Boric oxide
4 Zinc oxide

5 Sodium oxide
6 Fluorspar

Impact on Edge

B_2O_3	Na_2O	Na_3AlF_6	CaF_2	$NaSbO_3$	ZnO
..	..	0.184	0.161	0.164	0.178
..	0.184	..	.161	.177	.185
..	.161	.161	..	.198	.208
..	.164	.177	.198	..	.181
..	.178	.185	.208	.181	..
0.184	..	..	.255	.167	.185
.161	..	.255	..	.161	.183
.164	..	.167	.161	..	.181
.178	..	.185	.183	.181	..
.161	.255	..	..	.175	.186
.177	.167	..	.175	..	.175
.185	.185	..	.186	.175	..
.198	.161	.175	..	..	.166
.208	.183	.186	..	.166	..
.181	.181	.175	.166	..	..
.180	.182	.185	.185	.175	.183

Rating

1 Fluorspar
2 Cryolite

3 Zinc oxide
4 Sodium oxide

5 Boric oxide
6 Sodium antimonate

Impact on Center

B_2O_3	Na_2O	Na_3AlF_6	CaF_2	$NaSbO_3$	ZnO
..	..	0.362	0.337	0.325	0.343
..	0.362	..	.387	.456	.450
..	.337	.387	..	.475	.500
..	.325	.456	.475	..	.325
..	.343	.450	.500	.325	..
0.362	..	..	.337	.331	.331
.337	..	.337	..	.325	.387
.325	..	.331	.325	..	.331
.343	..	.331	.383	.331	..
.387	.337	..	..	.356	.393
.456	.331	..	.356	..	.331
.450	.331	..	.393	.331	..
.475	.325	.356	..	..	.387
.500	.387	.393	..	.387	..
.325	.331	.331	.387	..	..
.396	.341	.373	.388	.364	.378

Rating

1 Boric oxide
2 Fluorspar

3 Zinc oxide
4 Cryolite

5 Sodium antimonate
6 Sodium oxide

TABLE V *(continued)*

Average for the Series (all tests)

1 Fluorspar
2 Boric oxide

3 Sodium antimonate
4 Zinc oxide

5 Cryolite
6 Sodium oxide

RESULTS WITH CHANGES IN COMPOSITION
Series III

Type	Variables common to type enamel	Thermal Test (*A*) Boric oxide (B_2O_3)	(*B*) Sodium oxide (Na_2O)	(*C*) Cryolite (Na_3AlF_6)	(*D*) Fluorspar (CaF_2)	(*E*) Sodium antimonate ($NaSbO_3$)	(*F*) Zinc oxide (ZnO)
AB	B_2O_3—Na_2O	..	..	13	13	14	15
AC	B_2O_3—Na_3AlF_6	..	13	..	15	15	14
AD	B_2O_3—CaF_2	..	13	15	..	15	11
AE	B_2O_3—$NaSbO_3$	..	14	15	15	..	15
AF	B_2O_3—ZnO	..	15	14	11	15	..
BC	Na_2O—Na_3AlF_6	13	..	..	12	11	13
BD	Na_2O—CaF_2	13	..	12	..	13	11
BE	Na_2O—$NaSbO_3$	14	..	11	13	..	14
BF	Na_2O—ZnO	15	..	13	11	14	..
CD	Na_3AlF_6—CaF_2	15	12	..	..	15	15
CE	Na_3AlF_6—$NaSbO_3$	15	11	..	15	..	15
CF	Na_3AlF_6—ZnO	14	13	..	15	15	..
DE	CaF_2—$NaSbO_3$	15	13	15	..	..	14
DF	CaF_2—ZnO	11	11	15	..	14	..
EF	$NaSbO_3$—ZnO	15	14	15	14	..	..
	Average	14	12.9	13.8	13.4	14.1	13.7

Rating

1 Sodium antimonate
2 Boric oxide

3 Cryolite
4 Zinc oxide

5 Fluorspar
6 Sodium oxide

Acid Test (*A*) B_2O_3	(*B*) Na_2O	(*C*) Na_3AlF_6	(*D*) CaF_2	(*E*) $NaSbO_3$	(*F*) ZnO
..	..	60	60	60	60
..	60	..	60	60	60
..	60	60	..	60	60
..	60	60	60	..	60
..	60	60	60	60	..
60	..	..	60	60	60
60	..	60	..	60	60
60	..	60	60	..	60
60	..	60	60	60	..
60	60	..	..	60	60
60	60	..	60	..	60
60	60	..	60	60	..
60	60	60	..	..	60
60	60	60	..	60	..
60	60	60	60	..	..
60	60	60	60	60	60

Opacity B_2O_3	Na_2O	Na_3AlF_6	CaF_2	$NaSbO_3$	ZnO
..	..	9	5	5	4
..	9	..	4	5	6
..	5	4	..	2	1
..	5	5	2	..	2
..	4	6	1	2	..
9	..	..	3	4	6
5	..	3	..	1	5
5	..	4	1	..	1
4	..	6	5	1	..
4	3	..	..	6	4
5	4	..	6	..	5
6	6	..	4	5	..
2	1	6	..	..	2
1	5	4	..	2	..
2	1	5	2	..	..
4.3	4.3	5.2	3.3	3.3	3.6

Ratings

Not affected by the treatment.

Ratings

1 Cryolite
2 Sodium oxide

3 Boric oxide
4 Zinc oxide

5 Sodium antimonate
6 Fluorspar

Impact on Edge

B_2O_3	Na_2O	Na_3AlF_6	CaF_2	$NaSbO_3$	ZnO
..	..	0.188	0.209	0.202	0.180
..	0.188	..	.173	.169	.178
..	.209	.173	..	.194	.172
..	.202	.169	.194	..	.184
..	.180	.178	.172	.184	..
0.188	..	..	.169	.184	.168
.209	..	.169	..	.173	.177
.202	..	.184	.173	..	.169
.180	..	.168	.177	.169	..
.173	.169	..	..	.181	.191
.169	.184	..	.181	..	.177
.178	.168	..	.191	.177	..
.194	.173	.181	..	..	.175
.172	.177	.191	..	.175	..
.184	.169	.177	.175	..	..
.185	.182	.179	.181	.181	.177

Ratings

1 Boric oxide
2 Sodium oxide

3 Fluorspar
4 Sodium antimonate

5 Cryolite
6 Zinc oxide

Impact on Center

B_2O_3	Na_2O	Na_3AlF_6	CaF_2	$NaSbO_3$	ZnO
..	..	0.306	0.425	0.406	0.325
..	0.306	..	.450	.400	.394
..	.425	.450	..	.381	.387
..	.406	.400	.381	..	.319
..	.325	.394	.387	.319	..
0.306	..	..	.344	.356	.294
.425	..	.344	..	.256	.376
.406	..	.356	.256	..	.375
.325	..	.294	.376	.375	..
.450	.344	..	..	.331	.400
.400	.356	..	.331	..	.456
.394	.294	..	.400	.456	..
.381	.256	.331	..	..	.306
.387	.336	.400	..	.306	..
.319	.375	.456	.306	..	..
.379	.346	.373	.366	.359	.363

Ratings

1 Boric oxide
2 Cryolite

3 Fluorspar
4 Zinc oxide

5 Sodium antimonate
6 Sodium oxide

Average for the Series (all tests)

1 Boric oxide
2 Cryolite

3 Sodium antimonate
4 Fluorspar

5 Sodium oxide
6 Zinc oxide

regard to the effect of that difference. We may say, then, that in an *AB* type enamel, *C* produces a different effect than either *D*, *E* or *F*.

The next type of enamel would be the *AC* type with *B*, *D*, *E* and *F* as the differing constituents, thus—*ACB*, *ACD*, *ACE* and *ACF*. It is at once apparent that in an *AC* enamel, *B* produces a different effect than *D*, *E* or *F*. Following this procedure, the effects produced by the six variables may be compared and rated (Table V). Each enamel is used in three different comparisons for each test because each group of four enamels represents a distinct type and each enamel of that type is entitled to consideration regardless of the fact that it also falls in another type group.

From Table V it may be seen that the substitution of one constituent for another may improve an enamel of one type but not of another. There are ten comparisons for each constituent and by averaging the values they may be rated as to their general behavior in the particular test under consideration.

Sodium and boric oxides, which are not usually regarded as opacifying agents, are given ratings on their *ability to contribute* to the opacity. This ability was found to be greater in some cases than that of materials which are ordinarily considered as such. Although this result is contrary to general belief, it does not present an entirely new idea; in fact, such a possibility was discussed by R. C. Purdy and R. T. Stull[1] in 1908. It is believed that the greater fluidity resulting from the use of these two oxides allows a more complete dispersion of the included opacifying materials and that boric oxide may act to some extent as a mineralizer.

Although, as previously stated, it is evident from Table V that an ingredient which is beneficial in one enamel may have a detrimental effect in another, this fact does not necessarily indicate that the ingredient acts in an inconsistent way, nor does it conflict seriously with the theory that an enamel is a solution[2] (usually one containing suspended particles), the properties of which are approximately additive functions of the properties contributed by the individual constituents. The apparent discrepancy between these results and the theory is probably due to numerous indeterminate reactions which take place during the smelting of an enamel and its application.

The fact that a constituent does not always produce the same apparent effect in enamels of different composition makes any generalization difficult and any inconsistencies noted can reasonably be attributed to our lack of information regarding the constitution of materials of this type. There are, nevertheless, several general conclusions that may be drawn from the data in Table V.

For each series a list of the variable constituents, arranged in order of their general value in the enamels, has been prepared by taking the average rating of each material for all the tests. It seems that from such lists an idea may be obtained concerning the extent to which this average may be trusted to show the effect of any constituent when it is introduced in any particular enamel. In Series I, for instance, the first three constituents on such a list would be sodium antimonate, zinc oxide and sodium oxide. The enamel containing these three was No. 16 (Table II). This enamel did, in general, yield better results under the tests than any other in the series; however, it was a matt enamel. Further, the enamel containing the three constituents with low ratings was No. 5, which was among the four enamels having the poorest general standings in the series. On the other hand, such an analysis of the data would not indicate that the enamel containing sodium antimonate, sodium oxide and cryolite as variables (No. 12) would make an even poorer general showing than enamel No. 5.

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[1] "A Cheap Enamel for Stone Ware," R. T. Stull, Discussion, *Trans. Amer. Ceram. Soc.*, **10,** 225 (1908).

[2] H. F. Staley, *Jour. Amer. Ceram. Soc.*, **7** [10], 719 (1924).

In Series II the enamel containing the three high rating constituents was No. 8, which lacks only one place of being the best of the series in the tests. The enamel containing the three constituents of low rating (No. 13) was again among the poorest of the series.

The enamel containing the three constituents with the best average ratings in Series III is No. 6. It is among the better enamels, but is equalled or excelled in general by seven others of the series. Moreover, enamel No. 15 containing the three materials with low ratings is as good in general as the average of Series III.

Apparently, therefore, although lists can be compiled showing the average relative behavior of different ingredients, too much dependence cannot be placed upon them for guidance in determining the behavior of any particular combination of ingredients.

Considering one test at a time, the data in Table V permit of some interesting comparisons. The results of the thermal tests form a very definite basis for dividing the six variable constituents into three groups according to their contribution toward resistance to failure in this test. The agreement is good in all three series, except for cryolite, which is slightly irregular in Series III. The groups are: first, boric oxide and sodium antimonate; second, zinc oxide and fluorspar; and third, cryolite and sodium oxide. An average of the results in this test of all three series gave the six in the order named. It is interesting to note that the order is one of increasing expansivity factor with the single exception of sodium antimonate, which is doubtful. The factor for sodium antimonate has never been determined and must, therefore, be calculated from the factors for the constituent oxides.

In the acid test no comparative figures for the different variable constituents were obtained in Series III, because no enamel in that series was affected by the treatment. The results for Series I and II, however, agree very well. Sodium antimonate, fluorspar, sodium oxide and boric oxide are first, second, third and fifth respectively in both series, while cryolite and zinc oxide vary between fourth and sixth.

In the ratings for the three series according to opacity there are three noticeable irregularities, but these are not enough to upset the general order which would correspond to an average of the three series. Cryolite rates much lower in Series I than in II and III, sodium oxide rates higher in Series III than in I and II, sodium antimonate rates lower in Series III than in Series I and II. Since each rating must be considered as indicating the action of the constituents of the kind of enamel used in the corresponding series, the value of a rating representing the average of all three series is doubtful. It is of interest, however, that with respect to opacity, the order prevailing in such an average would exactly coincide with the order in Series II, which represents most nearly the ordinary commercial type of enamel.

The ratings for mechanical impact show no consistency between the three series (Table V). In Series I, however, the order for impact-on-edge is the reverse of the order of the quenching test. This is in accordance with the theory herein advanced concerning the effect of expansivity on resistance to these tests. Furthermore, the orders for impact-on-center of Series II and III are very similar to those of the quenching test, a fact which also supports the theory. In Series II and III for impact-on-edge, and in Series I for impact-on-center, the order of expansivity factors corresponding to the oxides is irregular. Attention is again called to the fact that the expansivity is believed to be only one of the major factors affecting these properties of the enamels.

Conclusions

This paper deals entirely with white cover enamels applied to a standard ground coat of relatively low coefficient of expansion which is typical of commercial practice. The following conclusions are based on results obtained:

1. The coefficient of expansion is only one of the major factors affecting the ability of enamels to resist mechanical and thermal shock.
2. Resistance to quenching and to impact on parts of ware free to deflect, increases with decreasing expansivity of the enamels.
3. Resistance to impact on a curved surface, or part of ware not free to deflect, increases slightly with increasing expansivity.
4. Boric oxide and sodium oxide are conducive to greater opacity in some enamels when these constituents are substituted for a part of some of the materials ordinarily used as opacifying agents.
5. Replacing the customary flint content of the enamels by feldspar increases the resistance to impact-on-edge and decreases the resistance to impact-on-center, decreases opacity and resistance to quenching and acid attack.
6. In most cases replacing the usual feldspar content of the enamels by flint greatly increases resistance to quenching and acid attack and decreases opacity. This also slightly decreases resistance to impact on edge and center.
7. Enamels containing both silica and feldspar were, on the whole, most satisfactory for general use, but enamels having certain excellent proper-

ties, making them more suitable for special purposes, were found in Series I and III.

8. While generalities may be drawn regarding the usual effect of substituting certain constituents for others in an enamel, this effect sometimes varies with the type of enamel used.

NOTE: The authors are indebted to the Coonley Manufacturing Co. for the supply of steel dinner plates used in this work, also to T. D. Hartshorn for help in preparing and testing the enamels.

THEORY OF COAL MEASURE FIRE CLAYS[1]

By Ellis Lovejoy

I. Purification by Vegetation

Theory of Purification by Vegetation

The theory that coal measure fire clay deposits are clay beds purified by the growth of coal producing vegetation is very far from satisfactory and teachers of geology present it to their students with an apology for its weakness.

Quantity of Vegetation Growth Required

It is said that an inch of coal required a foot of peat and a much greater thickness of accumulation of the original vegetation. If this is approximately true, then a foot of coal required 12 feet of peat; 6 feet of coal required 72 feet of peat, and considerably over one hundred feet accumulation of the original vegetation. It is very doubtful if the roots of the growing vegetation (perhaps I should say rootlets) reached to such a depth in any great number; certainly, purification of the clay bed would practically cease when the depth of vegetable remains equaled the length of the roots of the growing vegetation.

If the theory of purification by vegetation is true and if it is assumed that the underlying soil was the same in each instance, then the majority of fire clay beds should have approximately the same thickness. The soil on which the beds grew could not be the same in character. The penetration of the roots would be much greater in some soils than in others. Where the penetration was shallow the clay beds should have been purified to a greater degree, but only to the depth of root penetration.

Clay Partings Not Purified

Sections of coal in geological reports show clay, soapstone (clay), and shale partings, which frequently are as thick as many fire clay beds under the coal. These partings were the soil in which grew the coal resting upon them. There evidently was no lack of sustenance for the subsequent coal growth nor are these partings pure clay, usually quite the contrary. The shale partings have not been purified nor have the lamination planes been broken up.

Clay Soil Not Necessary to Vegetable Growth

In two instances which have come to my attention, the partings were sandstone. The top coal must have grown in this sandstone and it seems evident in these instances that a base soil is not essential to the growth of coal vegetation.

The vegetation grew in swamps largely on vegetable muck, drawing the mineral salts from the water and decaying vegetation instead of from the underlying soil.

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[1] Recd. Aug., 1925.

No Relation between Thickness of Coal and of Clay

On the theory of purification of fire clay beds by vegetable growth, thin beds of coal should be accompanied by thin beds of fire clay, and thick beds of coal should overlie correspondingly thick fire clay. To the contrary a mere streak of coal,[1] may have six to twelve feet or more of fire clay. The thick beds of coal are not notable for their fire clays. The Pittsburgh, and the Middle Kittanning ("Big Vein") in the Hocking Valley have clay of little value whereas the Lower Kittanning with a coal often too thin to be workable has a wonderful fire clay bed, likewise the Clarion and Tionesta.

The theory was bolstered by the explanation that the coals have been eroded and that the present coal thickness bears no relation to the thickness of the underlying clay. This is a weak prop in view of the fact that thin coals extend over wide areas and they are quite as regularly thin as are the thicker coals thick. The thin coals as well as the thick coals are often covered by clay-shales and limestones which are not erosive since they were deposited in quiet waters.

Practically all the valuable fire clay beds are in the lower coal measures of the Appalachian basin which would not be the case if the theory had any ground in fact.

The old theory is untenable and should be abandoned whether we have a better explanation or none at all.

I. Clay, the Residual of Plant Decay

Wilbur Stout, of the Ohio Geological Survey, presented a new and unique theory; in brief,[2] that the clay beds are residual oxidized coal, or peat, namely, hydrated coal ash, and include altered foreign sediments, which explains the vagaries relative to the thickness of the clay beds and related coal beds. It also explains the quite close chemical composition of the numerous clay beds, and the physical structure.

The theory tersely stated by Mr. Stout is (Geological Survey of Ohio, Fourth Series, Bulletin 26):

> Under the theory outlined many of the relationships of clay to coal are easily explained. They were both swamp deposits formed during the periods plant life flourished there. The coals were derived directly from vegetable matter and the clay from terrigenous sediments augmented slightly by plant residues, both highly altered by the action of vegetation and its products of decay and by the action of various other reagents effective under such conditions.
>
> The clay deposits were gradually built up, thus receiving the maximum amount of purification. There was no break in the plant life, only a shifting of conditions from

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[1] Often none at all except a stain nor even this in some instances.

[2] W. Stout, "Theory of the Origin of Clays," *Trans. Amer. Ceram. Soc.*, **17**, 557 (1915).

decay to preservation or from clay-forming to coal-forming stages. The quality of the clay is accounted for by the rate of deposition of sediments, the intensity of the chemical reactions, the duration of time such processes were effective, the condition of the water whether salt or fresh. In general, the theory explains satisfactorily the geological, chemical and physical features of clays, and harmonizes with the facts observed in the field.

Criticism of Stout's Residual Theory That some fire clay deposits are stratified is the most pertinent objection to the theory as presented.[1]

Discussing Stout's theory,[2] it was stated that fire clays commonly were more sandy in the bottom. There are many exceptions to this rule of fire clay deposits being more sandy in the bottom. A notable exception is the Clarion clay in northern Pennsylvania where in a very limited area there is sandy clay in the top, in the middle and in the bottom. Sometimes the three sand stratas are interstratified with the more plastic clay.

Fire clays as a rule do not have stratification planes, neither do many sandstones nor rock shales in strata equivalent in thickness to fire clay beds. The fire clays are quite regular in thickness over wide areas and have definite floors and roofs, and an occasional bed is definitely stratified.

It is difficult to conceive that residual oxidized swamp deposits including terrigenous material could have the regularity of the fire clay deposits. It is also difficult to conceive that in every fire clay bed we would not find frequent inclusions of lenticular beds of coal which had escaped the oxidation, yet such inclusions are extremely rare.

If either the purification or residual theory is fully true, fire clay should be found under peat beds, but districts where peat abounds are not producers of fire clays.

III. Fire Clays as Altered Sedimentary Material

The vegetation in the great coal basin grew as a fringe around the basin and likely on islands within the basin, advancing as the basin filled with sediment or as the floor of the basin was elevated by seismic disturbances. In major subsidences the swamp growth was buried under masses of rock sediments (representing the intervals between the coal beds) and another swamp developed when the conditions were made favorable by subsequent elevations.

It is a reasonable assumption that the fire clay beds are truly stratified; that they are the flotsam and jetsam from the great fringe, floating out into the basin and building up a deposit to the water level and thus preparing the way for the advance of the vegetable growth.

The basin was of great extent, with internal currents, subject to low tides, and variously agitated by winds and waves, thus keeping the more or less flocculent clay material floating, spreading it farther and farther out into the basin.

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[1] G. H. Ashley, *Jour. Amer. Ceram. Soc.*, **2** [10], 790 (1919).

[2] *Loc. cit.*, **17**, 557 (1915).

Torrential rains flooded the swamps with sediments. The vegetation digested these sediments, disintegrated them, and added its quota of oxidized residue to them. The ebb carried these sediments and the waste of the vegetation out into the basin. Thus were the fire clay beds formed distinctively different from the beds of shale and sandstone which accompanied them. The latter are purely sediments swept into the basin direct from the upland while the former have gone through the swamp belt and been purified. Both, however, are sedimentary in origin.

Since the fire clay sediments were largely flocculent they would be slow in settling and since they would be less intermittent than the simple flood sediments, we would not expect them to settle in laminae as do the shale sediments; instead we would get the structureless mass of a fire clay. In a number of instances, however, fire clays are decidedly shaley in structure which is evidence of their sedimentary origin.

It seems a bit significant that the greater fire clay beds are in the lower measures. As the basin filled with sediments it became smaller and likely shallower. Instead of a great basin fringed with a wide border of advancing vegetation, it became more nearly a swamp throughout its area, with long wide promontories reaching out into the area, many islands, large and small, dividing the area into a series of stagnant lakes, eliminating any tidal movement, reducing the wave action, and curtailing the currents. Under such conditions the sediments from the coal growth would have only limited opportunity to build up large and wide reaching deposits, while on the other hand we must strain a point to assume that residual oxidized material had not a development opportunity equal to that in the lower measures.

If peat bogs are not underlaid by clay may it not be due to the fact that the basin was small and did not permit sedimentation, yet the small size would not prevent residual oxidized material? Fire clay beds do not seem to me to be simple upland sediments, nor are they such sediments purified by the growth of vegetation on them, instead they are upland sediments which have come down through the swamp and perhaps undergone some alteration by contact with the swamp growth and decay, particularly in the iron minerals, together with waste sediments from the swamp itself. In some beds the altered sediments may predominate, and in others the swamp waste.

I take this to be Stout's theory. In some instances these swamp sediments may be intermingled with simple upland sediments entering the basin through direct channels.

The beds are not residual deposits, instead they are stratified sedimentaries which have drifted out into the basin in advance of the coal growth, and have developed the condition for the extension of the vegetation. The swamp vegetation is the mother bed of the fire clay beds.

IV. Application of Sedimentary Theory

The clay in Southern Ohio underlying the lower Mercer limestone, and formerly known as the Lower Mercer fire clay, is now designated as the Middle Mercer clay. Below this comes the Flint Ridge coal and fire clay. In some places, notably Union Furnace, Ohio, the two clays are together without the separating Flint Ridge coal, but with a dark streak which is probably the mark of the Flint Ridge coal. Elsewhere the two beds are separated by several feet of shale or sandstone.

Similarly the Tionesta and Brookville clays come together in some places and elsewhere are separated by shale up to fifteen or more feet.

At Oak Hill the flint clay rests on the Lower Kittanning coal, and both it and the plastic clay under the coal are worked. At Hamden, Ohio, the Oak Hill coal is over a foot or more of the Oak Hill flint clay, below which is the Lower Kittanning coal underlaid by a deep bed of the Lower Kittanning clay. These beds are contiguous. In other localities the two members in the scale are separated by 15 to 20 feet of shale.

The Middle Mercer and Flint Ridge clays are very much alike. The Tionesta and Brookville are notably different, especially in weathering characteristics.

The Oak Hill and Lower Kittanning in the Oak Hill district are totally different, one being a flint clay and the other a sandy plastic clay.

Explanation by Stout's Theory

Under Stout's theory, in each instance where the beds are contiguous, the growth of the vegetation is assumed to have been continuous and with this, where no streak of coal separates the beds, the oxidation to have been coincident with the vegetable growth. Where the coal intervenes, oxidation would have ceased and preservation prevailed for a time, followed by oxidation and the period closed with preservation and final submergence.

Where shale or sandstone splits the beds, the development of the lower bed in each case is assumed to have ceased and elementary sediments covered it, followed by subsequent growth of vegetation over the sediments. This involves local subsidence and subsequent elevation.

Explanation by Sedimentation Theory

It seems more reasonable to assume that these beds are altered sedimentaries instead of residuals. At the close of each period of the lower bed there was some elevation, permitting the vegetation to advance over the accumulated sediments and thus develop the streak of coal or its mark. This was followed by subsidence. The influx of elementary sediments which would follow filled the hollows in the underlying altered sediments until equilibrium was established, then coal-forming material again accumulated building up the second bed on the underlying shale and clay sediments. Thus we would have the later bed of fire clay in some places resting immediately on the lower bed and elsewhere there would be an intervening belt of shale or sand.

The period closes with either the filling of the basin in front of the coal growth to permit the advance of the vegetation over the sediments, or by elevation of the clay to the water level thus permitting coal growth, and finally submergence, followed in the instances of the Lower Mercer and the Brookville by limestone formation. The following quotation[1] is pertinent.

> In the Appalachian fields the Pittsburgh, Waynesburg and Washington, in the upper portion of the series, approach as nearly to continuity as one may conceive, for they are always present in exposures and records within an area of thousands of square miles; but the Pittsburgh shows remarkable variations in thickness; it thins away to nothing from all sides toward the central part of the area, while at times only its under clay remains to mark the horizon.

It cannot be assumed that the Waynesburg and Washington swamps were from the beginning covered with vegetation, instead from the very nature of swamps the growth was a net work of vegetation enclosing lagoons and lakes which gradually filled with the waste from the vegetation and as the filling proceeded the vegetation closed in.

May it not be that the under clay which "remains to mark the horizon" of the Pittsburgh is the advanced front of the clay sediment which did not come to the surface to permit the growth of the coal over it, and is it not evident that smaller swamps did not possess essential conditions for large beds of fire clay?

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[1] J. J. Stevenson, "Formation of Coal Beds."

COMPARISON OF METHODS USED IN ESTIMATING THE MATURING OF TERRA COTTA[1]

By Louis Anderson

ABSTRACT

The purpose of this investigation is to develop some means to better determine the maturing of terra cotta ware in the firing.

These tests were made at the American Terra Cotta Company's plant in a down-draft kiln. The kilns were fired from 110 to 120 hours, a Thwing pyrometer showing about 1115°C at the finish. The pyrometer was located half-way between the bottom and top of the kiln and within a few inches from any of the test pieces and cones.

Test Number 1

The first test made was to compare Orton cones, Mayer cones, red slip trials used by the Midland Terra Cotta Company and shrinkage trials used by the American Terra Cotta Company.

The red slip trials used by the Midland Terra Cotta Company are made of a regular body mixture dipped in red slip. The temperature is determined by the color; the greater the heat the darker they are.

The shrinkage trial used by the American Terra Cotta Company is a regular body clay free from grog and dry pressed into a wedge-shaped piece. The only moisture in the clay when pressing into shrinkage test piece is that which it contained at the time of grinding. The gage used to measure this shrinkage is graduated to .1%.

At about 1100°C with the kiln progressing about 3° an hour the first red slip and shrinkage trials were drawn and cones read. This was repeated every two hours until the finish of the run.

Result The red slip trial changed in color every two hours until two hours previous to the highest temperature. From this time on, it was possible to arrange the trials in the order in which they were taken from the kiln by the texture rather than by the color.

The shrinkage trials showed a fairly gradual shrinkage up to the highest temperature and for four hours after fires were drawn and the pyrometer had started down.

Mayer cones No. 3 continued to advance for two hours after the shrinkage trials stopped. One of the Mayer No. 3 cones did not start until the other was nearly down. At this time the shrinkage trial stopped, Orton cone No. 4 was bent and remained in this position.

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[1] Presented at the Annual Meeting, American Ceramic Society, Feb., 1925. (Terra Cotta Division.)

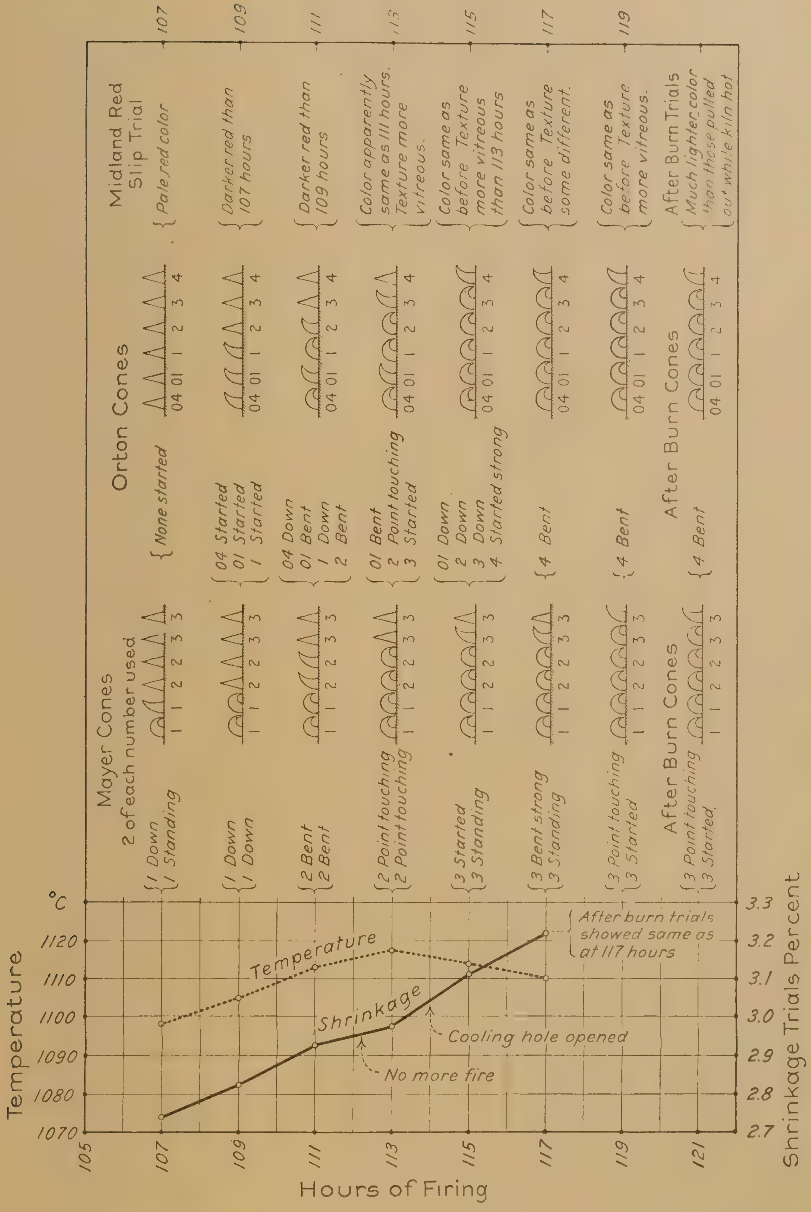
Mayer Cones
2 of each number used
1 1 2 2 3 3
1 Down
1 Standing
1 Down
1 Down
2 Bent
2 Bent
2 Point touching
2 Point touching
3 Started
3 Standing
3 Bent strong
3 Standing
3 Point touching
3 Started
After Burn Cones
3 Point touching
3 Started
Orton Cones
04 01 1 2 3 4
None started
04 Started
01 Started
1 Started
04 Down
01 Bent
1 Down
2 Bent
01 Bent
2 Point touching
3 Started
01 Down
2 Down
3 Down
4 Started strong
4 Bent
4 Bent
After Burn Cones
4 Bent
Midland Red
Slip Trial
Pale red color
Darker red than 107 hours
Darker red than 109 hours
Color apparently same as 111 hours. Texture more vitreous.
Color same as before. Texture more vitreous than 113 hours
Color same as before. Texture some different.
Color same as before. Texture more vitreous.
After Burn Trials
Much lighter color than those pulled out while kiln hot
107
109
111
113
115
117
119
°C
Temperature
1070
1080
1090
1100
1110
1120
Temperature
Shrinkage
No more fire
Cooling hole opened
After burn trials showed same as at 117 hours
Hours of Firing
105
107
109
111
113
115
117
119
121
Shrinkage Trials Percent
2.7
2.8
2.9
3.0
3.1
3.2
3.3

FIG. 1.

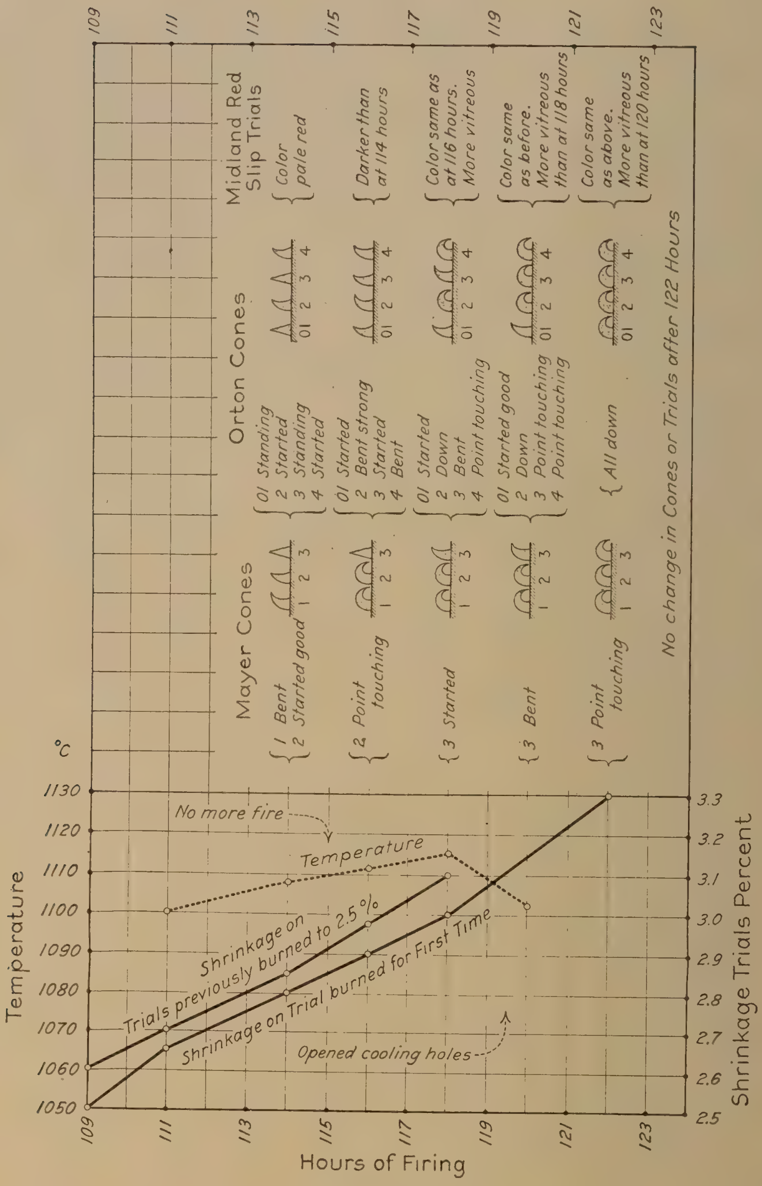
Temperature
°C
1050
1060
1070
1080
1090
1100
1110
1120
1130
Hours of Firing
109
111
113
115
117
119
121
123
Shrinkage Trials Percent
2.5
2.6
2.7
2.8
2.9
3.0
3.1
3.2
3.3
No more fire
Temperature
Shrinkage on Trials previously burned to 2.5%
Shrinkage on Trial burned for First Time
Opened cooling holes
Mayer Cones
Orton Cones
Midland Red Slip Trials
1 Bent
2 Started good
1 2 3
01 Standing
2 Started
3 Standing
4 Started
01 2 3 4
Color pale red
2 Point touching
1 2 3
01 Started
2 Bent strong
3 Started
4 Bent
01 2 3 4
Darker than at 114 hours
3 Started
1 2 3
01 Started
2 Down
3 Bent
4 Point touching
01 2 3 4
Color same as at 116 hours. More vitreous
3 Bent
1 2 3
01 Started good
2 Down
3 Point touching
4 Point touching
01 2 3 4
Color same as before. More vitreous than at 118 hours
3 Point touching
1 2 3
All down
01 2 3 4
Color same as above. More vitreous than at 120 hours
No change in Cones or Trials after 122 Hours

FIG. 2.

Test Number 2

As a check on the first test, another was made to see the effect on the color of dipping the red slip trial, when hot, in water.

A comparison was made of shrinkage trials fired for the second time and a raw trial at various temperatures near the finish of the firing. The trials used were fired the first time at 1065°C or 2.5% shrinkage. The trials that were put in raw on the second firing showed 2.5% at 1060°C. The refired shrinkage trials showed an accumulation of shrinkage, it being 2.6% or .1% more than the shrinkage of the first fired trial. The refired trial continued to show a shrinkage of about .1% until three hours after the last firing of the kiln.

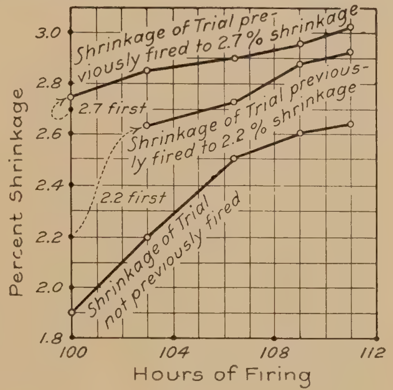

FIG. 3.

The red slip trials were broken in two, and one-half dipped in water while very hot. This apparently had no effect on the color aside from a few streaks of light scum. In other respects the red slip trials showed the same as the first test.

The shrinkage trials continued to shrink for four hours after the pyrometer had started down, at which time the Orton and Mayer cones stopped.

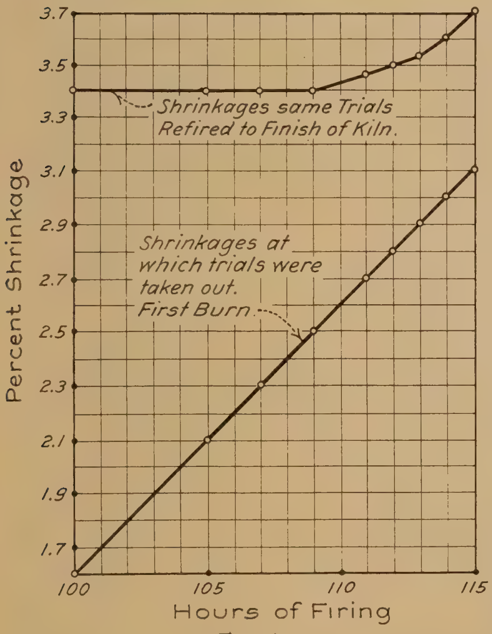

FIG. 4.

Test Number 3

The next test was a check on the refiring giving a greater shrinkage at the same heat or less. Trials going into the kiln for the second firing were previously fired to 2.2% and 2.7% shrinkage and were arranged to be taken out with trials which were in for the first time.

At the time when a regular trial showed 1.9% shrinkage, one which had been previously fired to 2.2% showed $2.6^1/_2$% shrinkage. The trials fired to 2.7% on the first firing advanced to 2.8$^1/_2$%. The refired trials continued to shrink more than .3% throughout the firing period and two hours of soaking.

Test Number 4

This test was made with shrinkage trials to determine what further shrinkage those in the first firing would have on a second firing if fired at about 1130°C. The trials were fired the first time at various shrinkages from 450°C to 1115°C.

These trials with some raw ones were placed in a sagger and fired in a regular way. The trials fired for the second time showed further shrinkage up to 1060°C which is 2.5% shrinkage. From 2.5 to 3.1% the shrinkage increased until the trials fired to 3.1% the first time, showed 3.7% on the second firing, instead of 3.4% shrinkage on trials in for only one firing.

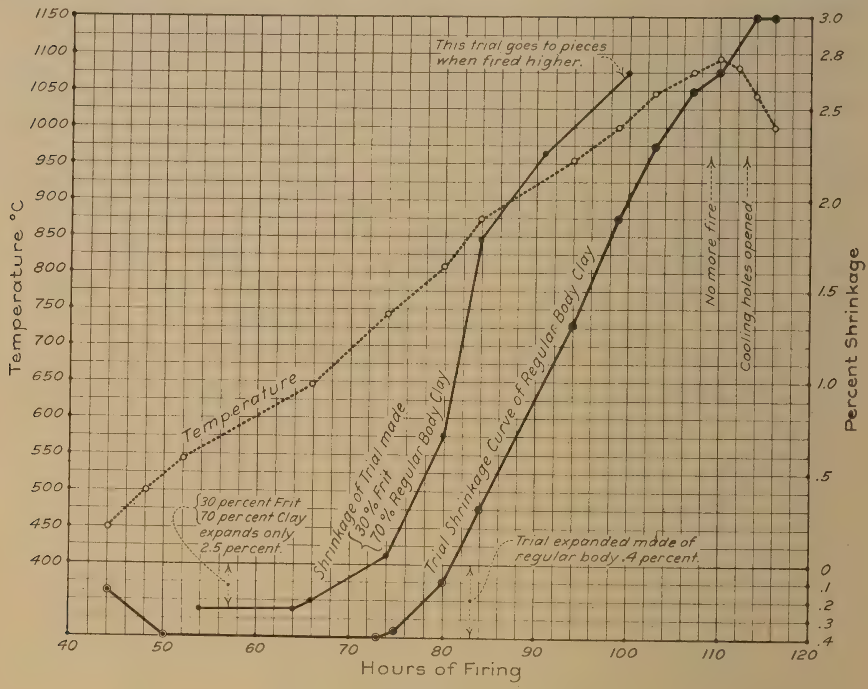

FIG. 5.

Test Number 5

We find a trial very useful composed of 70% body clay and 30% of frit ground fine.

The straight clay at 400°C contracts to .2%. At 450°C it starts to expand, there being .4% expansion at 525°C. It remains at this expansion until 775°C, at which time it again contracts reaching its original size at 825°C.

With the 30% frit the expansion of the trial is only .25%. It also shows a shrinkage about ten hours sooner than does the straight clay.

At 1025°C when the straight clay shows a shrinkage of 1.0% the frit trial shows 2.2%.

Conclusion

Previous to 1912 a red body, dipped in red slip, was used as a guide in firing. This was apparently not giving results.

A small trial was cast and used as a shrinkage trial. This trial proved to be so good that a machine was used to press them.

In 1916 the red slip trials were given another chance for about four months. We used these in connection with cones and shrinkage trials. The slip color, being so uncertain, the color trials were discontinued. I believe a mixture could be made so that the change in color could be determined much better than at present.

I found that a slip made with manganese as a coloring was the most sensitive to changes of heat.

A trial could be made with one end for shrinkage and the other for dipping. I would not care to rely on shrinkage trials alone, although I believe if these were made with the same pressure and with moisture reasonably even, they would be reliable. We regulate the evenness of the kiln by shrinkage trials. A couple of cones are used and taken into consideration when determining the finish. A shrinkage trial, fired not too high the first time, is used very nicely to place in kiln at different parts for measuring shrinkage after the kiln is unloaded. These differences in temperature in different parts of the kiln are good facts to know.

TERRA COTTA, ILLINOIS

NEW TYPE OF OXY-ACETYLENE FUSION FURNACE, WITH NOTES ON THE BEHAVIOR OF REFRACTORIES AT CONE 40[1]

By A. F. Gorton and W. H. Groves

ABSTRACT

The furnace described in this paper differs from the usual type of fusion furnace in that acetylene is used as fuel and the burner is applied vertically instead of horizontally. Advantages offered by this novel design are rapidity and uniformity of heating, convenience as regards regulation and observation of the cones, economy of operation and simplicity of maintenance.

Introduction

Recent experiments at the Bureau of Standards[2] and the Bureau of Mines[3] with the granular carbon resistor furnace and the Northrup induction furnace have aroused considerable interest in softening point furnaces of the electrically heated type. While electricity as a fuel has certain inherent advantages, most ceramists have preferred to put their trust in results obtained with gas-fired furnaces. It is well known that the electric furnace is speedy, convenient to operate, as regards temperature regulation, and capable of reaching very elevated temperatures. It is quiet-running, and does not require a stack; hence the operator may observe with considerable comfort the progress of the fusion. These advantages are all afforded perhaps to a greater degree by the induction type than by the more familiar granular carbon resistor. The most prevalent objection to the use of these furnaces is the injurious effect of the reducing atmosphere[4] necessarily associated with white-hot carbon or graphite, it being well known that the Seger cones as well as those of clay deform at temperatures much below the normal softening point, if carbon monoxide is present. Although the Bureau of Standards has shown[5] that reduction may be avoided by passing air or oxygen slowly through the furnace chamber, this requires much extra apparatus. The Arsem vacuum type of furnace, which employs a spiral graphite resistor, is not free from this reducing action, though it has been used by Kanolt[6] to effect the fusion of oxides at temperatures up to 2800°C.

The expense of the electrical equipment is perhaps a graver objection, especially as regards the Northrup type of induction furnace, which operates by means of condensers and other high-frequency circuit devices. The transformer and rheostat required for the ordinary granular carbon furnace are fairly expensive (about $250, according to Pendergast), though it must be acknowledged that the cost of power consumed per test is low. The question of portableness is also to be considered. Although fusion tests have been performed hitherto mostly in the laboratory, and not at the mine, it is advantageous to be able to transport the equipment, as Wilson[1] points out. The electric furnace is not very portable, being dependent on electric current which is not available everywhere. The acetylene furnace and gas tanks can easily be transported. Many industrial establishments lack the necessary power supply required to operate an electric furnace, for the reason that three-phase, 25-cycle current is very prevalent, and since the furnace operates on single-phase, it would be necessary to install an extra supply line, to keep from disturbing the balance of the main transformers.

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[1] A summary of this paper was presented at a meeting of the Chicago Section, American Ceramic Society, April 14, 1925. Recd. Aug. 10, 1925.

[2] W. L. Pendergast, *Jour. Amer. Ceram. Soc.*, **8** [5], 319–25 (1925).

[3] Andrews, Bole and Withrow, II, *Jour. Amer. Ceram. Soc.*, **8** [3], 171 (1925). Also P. D. Helser, "A Laboratory Load Furnace," to appear in *Jour. Amer. Ceram. Soc.*, December, 1925.

[4] Andrews, Bole and Withrow, *loc. cit.*, p. 185.

[5] Pendergast, *loc. cit.*

[6] Bur. Stand., *Tech. Paper* **10**.

The present furnace was designed for rapidity and uniformity of heating, rather than economy and portableness, though the latter are features that will appeal to many ceramists. The temperatures attainable with a furnace of this design exceed those claimed for pot furnaces fired with natural gas or oil, and the coke-fired Deville furnace. The limiting feature is probably the refractoriness of the plaque, since this part receives the full blast of the flame. The supporting pins also are subject to deformation above cone 40.

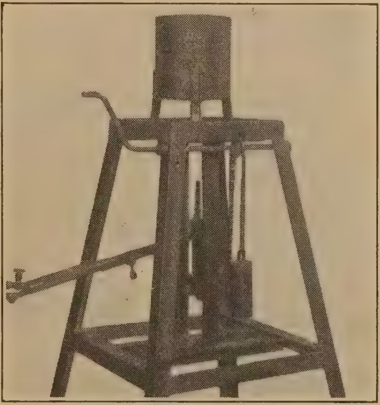

FIG. 1.

General Design

The furnace with stand and torch in position, ready to operate, is shown in the accompanying photograph (Fig. 1). This view shows clearly the smallness of the furnace proper relative to the height of the stand. The operator while seated may sight conveniently through the slot at the cones within the furnace chamber. At the same time the torch is within easy reach, so that he can make adjustment of the gas and work the counterpoise which raises and lowers the burner. Ordinarily, the gas mixture is adjusted but once, at the beginning of the run. For instance, if using a No. 10 tip, the oxygen is adjusted at ten pounds gage pressure, and the reducing valve on the acetylene is set to give a similar pressure. If the larger tip (No. 12) is being used, both oxygen and acetylene are adjusted at twelve pounds. Though our experiments so far have been conducted with acetylene and oxygen, it should be understood that oxy-hydrogen and natural gas-air or other gaseous fuels would be suitable, depending on the maximum temperature to be reached in the test. In fact, it would be desirable, for the sake of economy as well as for preservation of the lining, to preheat with natural or city gas.

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[1] Hewitt Wilson, "An Oxy-Acetylene High Temperature Furnace," *Jour. Amer. Ceram. Soc.*, **4**, 835 (1921).

Sectional View

The lining and the refractory pins which support the cone plaque are shown clearly in Fig. 2. The cones are symmetrically located near the periphery of the plaque proper, which rests on a supporting plaque, which in turn rests on the pins.

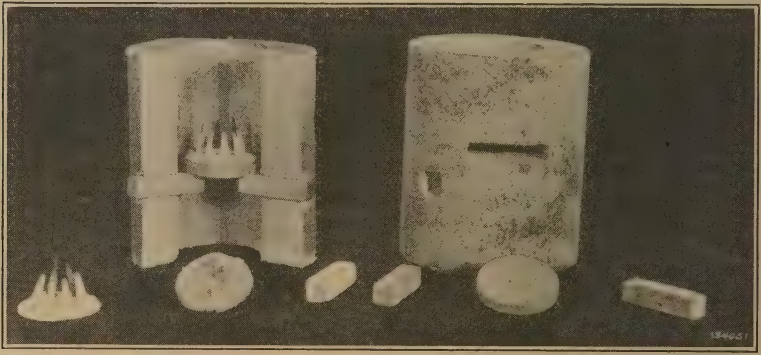

Fig. 2.

The pins are square in cross-section and fit loosely in square holes cut through the lining and steel shell, these holes being 120° apart, as shown. Although it is possible to replace a pin while the furnace is hot, experience shows that this is rarely necessary. Breakage of a pin during operation will tilt the plaque to a dangerous angle, but the cones will not upset. It is an advantage to be able to make the necessary repair by thrusting a steel rod up from below and supporting the plaque in this manner while a new pin is being substituted for the broken one.

Composition of Refractory Parts

Electrically fused (white) magnesia is the material used in forming the lining, plaque support and pins, although the "double dead-burned magnesite" is satisfactory provided cone 36 is not exceeded. Above cone 36 ordinary magnesite softens, due to the high iron content, and at cone 39 the pins and plaque support were found to warp badly. The lining was formed by tamping in a steel mold, the bond being milk of magnesia, or water. The plaques and pins were also "dry-pressed," using the same mixture. The amount of liquid should not exceed 5% by weight. As is well known, magnesite shapes are tender, or difficult to dry, and cracking is apt to develop. The preliminary firing should be done carefully in a small kiln and carried preferably to a temperature of 2600°F. The lining is thus under-fired at first, but after a few fusions the lining vitrifies on the inner surface. Since a furnace of these small dimensions loses heat rapidly through the side walls or "radially," there is a steep temperature gradient in this direction, which of course tends to preserve the steel jacket, as well as to prolong the life of the lining. Moreover, it appears desirable not to check this radial flow of heat by too thick insulation. We found that $^1/_4''$ soft asbestos was satisfactory as insulation between the lining and the steel jacket.

Supporting Stand and Torch Holder The base on which the furnace rests is of angle iron, acetylene welded. The height of the stand is 36″, and the floor area covered is 24″ x 24″. The height of the slot with furnace resting on the stand is 42″, hence is practically on a level with the operator's eyes. The torch holder consists of a steel plate bearing a projecting arm to which the torch is clamped. This plate slides easily in vertical guides, the total travel being 10″. The torch is raised and lowered by a chain which passes over a sprocket at the top and ends in a counterpoise. A handle is provided at the front for controlling the position of the torch. All these details are shown in Fig. 1.

The torch is a special model with tip bent at quite an angle, and is furnished by the Torchweld Equipment Company of Chicago. This company furnishes also the gages. The tip used is either No. 10 or No. 12, the latter being the larger size and more effective at high temperatures. Adjustment of the gage pressures is made such that if No. 10 tip is used, the oxygen and acetylene are each regulated to ten pounds pressure and similarly for the larger tip.

Visibility of Cones

As shown in the illustration, a slot in the front wall of the furnace affords the operator a clear view of the cones within the furnace chamber. It is thought that this feature, which can be appreciated only by those who have run fusion tests, distinguishes this apparatus from a great many fusion furnaces of the electric as well as gas or oil variety. In the old pot-furnace (gas-fired), it was necessary to lift the cover or baffle on top and peer in at quite an angle, in order to catch a glimpse of the white-hot cones. This is also necessary in the case of the granular-carbon and induction furnaces mentioned above. The same is true of Wilson's acetylene furnace. In the furnace here described, the reason why the cones show up so clearly is that the background or opposite wall is slightly cooler than the chamber proper and the cones, due to loss of heat radially as previously described. Hence the cones appear brighter than the lining.

Economy of Operation

A furnace of this type is practically a chimney, the hot gases being baffled, first by the plaque, and next by the baffle at the top of the furnace. Accordingly, the fusion chamber proper is comprised between the plaque and the top baffle—which is the hottest portion of the apparatus. Equilibrium at any temperature is characterized by an equality between the input of heat and the loss through the walls, top exit and by reflection from the bottom plaque. Although the furnace is very small, hence can be rapidly cooled or heated, it is easy to secure uniform heating of the plaque, since the full force of the flame is applied from below, in a vertical direction, and the flame sweeps upward around the edge of the plaque, uniting above the cones. Tests performed by placing 6 cones of the same number on a plaque showed equality of fusion at all points. Irregular results appeared only in case the rate of heating was excessive (*i. e.*, cone 30; in less than 20 minutes, starting from room temperature).

Several dozen tests of a wide variety of refractory substances have shown that the furnace is economical as well as speedy. After the first fusion, one naturally saves time because the plaque and lining are already hot, and it is possible to reach temperatures such as cone 36 in fifteen minutes. Cone 40 was the highest point reached, but this, of course, is not the upper limit. From our experience, we estimate that a fusion test will average about $0.30, including oxygen as well as acetylene. This figure exceeds that given for the electric furnace by Pendergast,[1] but equals the cost of operation of Wilson's acetylene furnace.

Results Obtained

A few typical results are given herewith:

	Cone
Tennessee Ball (J. P. No. 11)	33
English China Clay	32½
South Carolina Kaolin	34½
Cement ("Alumite")	35
Cement ("Arcofrax")	36½
Cement (chiefly Alundum)	39
Fire Brick ("American")	34
Fire Brick (E. & H. "Acme")	31
Fire Brick (Savage No. 1)	29½

Notes on Behavior of Refractories at Elevated Temperatures

At temperatures above that corresponding to cone 32, we observed interaction between the various refractory materials in close contact within the furnace chamber. Thus, fire clay and magnesia react to some extent beginning at cone 32, and alumina reacts with chrome above cone 36. Also, there is a zircon-magnesia reaction at about cones 37–38. It is this chemical action which makes difficult the determination of fusion points at elevated temperatures. Since we used magnesite for the supporting plaque, it was necessary to use a thin layer of chrome cement between this and the cone plaque, which was usually made of a mixture of alumina and kaolin. We noticed the familiar chrome-alumina pink tinge on cones and plaque when heating to cone 36 and above. A fusion test on zircon (zirconium silicate) failed for this reason, though a cone formed from a zircon brick (manufactured by Carborundum Company) showed some deformation above cone 32. It might almost be said that, at these elevated temperatures, a fusion test should be performed in a furnace where the lining, plaque, etc., are of the same composition as the material under test. Although, in this manner, chemical action would be avoided, objection might be raised on the ground that the refractories would suffer serious deformation during a single test.

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[1] *Loc. cit.*

Conclusion

In developing this new type of gas-fired fusion furnace, it has been our aim to take full advantage of the possibilities for rapid heating offered by the familiar acetylene torch, while at the same time retaining those features which ceramists have considered characteristic of gas-heated furnaces, namely, the oxidizing nature of the furnace atmosphere, and real uniformity of temperature throughout the furnace chamber. To these we have added convenience of regulation not excelled by the electric furnace, low cost of equipment and operation, and simplicity of maintenance. The operator can manage the furnace with a maximum of comfort, owing to the small size of the furnace and the small amount of radiation. A point especially noteworthy is the ease with which the cones may be viewed throughout the fusion period, due to the slot in the side of the furnace. Finally, this is the only fusion furnace which is portable in the strict sense of the word, since it can be carried easily in one hand.

The Western Electric Company, Incorporated, has applied for a patent covering those features of the furnace which are considered of sufficient novelty, namely, the mechanism for raising and lowering the burner, and the means for supporting the cone plaque.

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Chicago, Illinois

A MACHINE FOR TRANSVERSE TESTS OF CLAY AND GLASS LABORATORY SPECIMENS[1]

By A. C. Harrison

ABSTRACT

A machine for transverse testing which is easily adjusted, positive acting, and accurate for both light and heavy loads. Results are shown on vitreous china bodies and glass.

Introduction

This machine was designed to test the transverse breaking strength of clay and glass laboratory specimens of widely varying dimensions and strength. In order to test such specimens upon a single machine, it is essential to have high accuracy at both large and small loads and also means of varying the span and lever multiplying power. The machine is sufficiently flexible to test specimens varying from the smallest practicable size to one $2^1/_2'' \times 2^1/_2'' \times 21''$, and has satisfactory accuracy for direct loads varying from 2 to 1500 pounds. The Bureau of Standards[2] has recently developed three portable transverse breaking machines for testing whole brick, and various commercial machines[3] are also available which answer ordinary laboratory requirements for testing specimens of a practically uniform size and shape.

Description

General Description A beam and a lever (Fig. 2) constitute the active element of this machine. An adjustable counterpoise *C* and a weight *W* are suspended from the right-hand arm of the beam, and are approximately balanced by a bucket of shot *B* suspended from the left-hand arm and the weight of the lever acting through the connecting member *w* or *x*. An exact balance is accomplished by means of the counterpoise *C*.

Bucket and Valve The bucket is equipped with an automatically operated valve (Fig. 4) which controls the flow of shot. A scoop *R* (Fig. 2) catches the shot flowing from the bucket and a spring balance, supporting the scoop, registers its weight. The rate of flow of shot is regulated by placing special brass bushings in the valve, and any desired rate can be obtained by using a bushing of the proper inside diameter; however, only two have been found necessary. Two solenoids and three switches (Fig. 4) operate and control the valve. It opens, and starts the flow of shot, upon closing the electric circuit through a hand-operated spring contact F (Fig. 4); and it closes and stops the flow of shot, upon closing the circuit through another hand-operated spring contact S (Fig. 4), or through the automatic switch S' on the beam of the machine.

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[1] Printed by permission of the Director of the Bureau of Standards, Department of Commerce. Recd. Sept. 23, 1925.

[2] *Tech. Paper* **251**; *Bull. Amer. Ceram. Soc.*, **4** [8], 407(1925); *The Clay-Worker*, Feb. 28, 1925.

[3] The Olsen, Riehle and Fairbanks are among the foremost on the present-day market.

Valve Mechanism The valve mechanism indicated in Fig. 4 operates as follows: when slide a (actuated by solenoids s and s', for which the electric current is supplied by eight dry cells) occupies its extreme right-hand position, its orifice is in line with a similar one in the bottom of the bucket and shot is free to flow; and when the slide occupies its extreme left-hand position the orifices are not aligned and the flow is shut off. Hence, by energizing solenoid s' the slide is pulled to the right and shot begins to flow, and by energizing solenoid s the slide is pulled to the left and the flow is stopped. Upon beginning a test the valve is opened by means of switch F (Fig. 4), and upon failure of the specimen it is closed by means of the automatic switch S' (Fig. 4). The automatic switch is attached to the beam of the machine and closes when the beam falls below a horizontal position; consequently, upon rupture of a specimen, the clockwise rotation of the beam closes the switch and the flow of shot is quickly stopped.

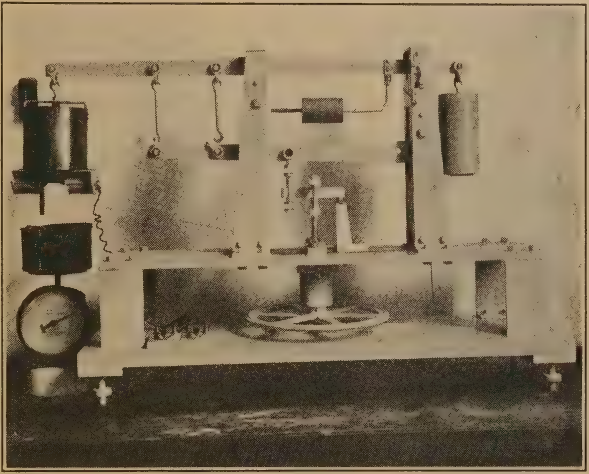

FIG. 1.—Showing lever combination of lowest multiplying power.

Straining Mechanism The straining mechanism (Figs. 1 and 2) is comprised of a wheel operating a screw to which a clevis is attached. Deflection of loaded specimens is compensated by rotating the wheel, thus keeping the beam level during tests. The photographs (Figs. 1 and 2) also show the machine set up with both the pulling clevis and connecting member attached to the lever in two different positions. The clevis and connecting member may be easily shifted from one to the other of these positions, thus providing a convenient means of changing the capacity of the machine. Its maximum capacity is 1500 pounds.

Lever Combination Four lever combinations having different multiplying powers can be made, and through them a wide range of forces can be applied at the pulling clevis. These combinations will be referred to as A, B, C and D and are described in Table I. With the beam (Fig. 3) initially balanced, the removal of shot from the bucket B produces an upward force at A proportional to the weight of shot removed. The resultant force applied to the specimen at the straining clevis depends upon the lever ratios employed.

Arrangement of Spans The machine is designed so that the straining mechanism can be placed and secured at any point between the beam and lever supports (a distance of $12^1/_2$ inches), and the fixed support can be similarly shifted between points c and d (Fig. 2) on the base. This arrangement is sufficiently flexible to permit the use of spans from 3 to 21 inches, a wide enough range for the usual clay and glass[1] laboratory specimens.

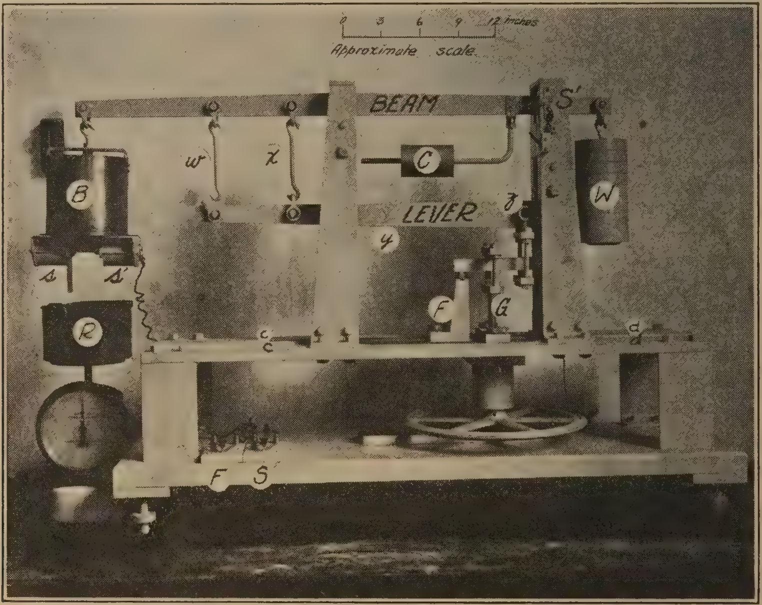

FIG. 2.—Showing lever combination of highest multiplying power.

Adjustment of Specimens A specimen to be tested is placed through the straining clevis with its ends resting upon the fixed support and pulling clevis.[2] The pulling clevis should be released (by raising the specimen slightly) and brought to rest in order to assure proper distance between the points supporting the specimen.

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[1] Williams, "The Mechanical Strength of Glazing Glass," *Jour. Amer. Ceram. Soc.*, **6** [9], 980 (1923).

[2] The straining and pulling clevis are large enough to test specimens of $2^1/_2'' \times 3''$ cross-section.

Operation

The beam is brought approximately to balance by pouring shot into the bucket until it is nearly equal in weight to W. A specimen is placed across the fixed support and pulling clevis, which is adjusted in the same manner described above, and the beam brought exactly to equilibrium by means of the counterpoise. Then the straining clevis is brought in contact with the specimen and the shot valve opened. The shot flowing from the bucket unbalances the beam, producing a gradually increasing active force at W which acts on the specimen and causes it to rupture; at the instant rupture occurs the valve in the bottom of the bucket is automatically closed. The beam is kept horizontal by means of the hand-wheel while the load is being applied. The weight of shot which has flowed out and which is indicated by the scale, is a measure of the force required to rupture the specimen.[1] The shot is returned to the bucket after each test and the machine is then ready for the next.

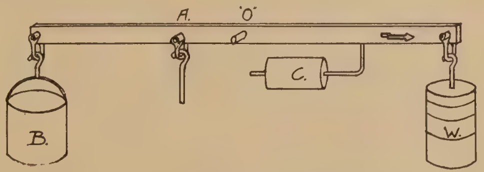

FIG. 3.—Showing the beam and its essential parts.

Calibration

As a means of calibrating the machine, a platform scale of comparatively low capacity and high accuracy replaced the fixed support. A rigid steel bar placed across the pulling and straining clevises transmitted the load to the scale, and a knife edge on the scale platform supported the fixed end of the bar. With the straining mechanism placed exactly midway between the points of support on the pulling clevis and scale, any force exerted upward by the pulling clevis was transmitted to the scale with no alteration in value. Each lever combination was calibrated by determining the respec-

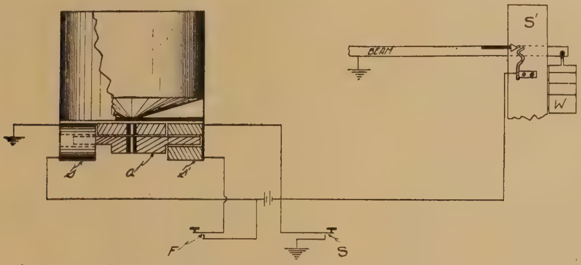

FIG. 4.—Showing the bucket, valve mechanism and electrical equipment.

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[1] The dial of the scale could be calibrated to show directly the force applied at the specimen. It would be necessary to have a scale for each lever combination.

tive weights of shot required to produce each of a series of loads on the scale. The values so obtained were then corrected for the time lag of operation of the switch. This lag was determined experimentally and found to be sufficiently constant for a given load and lever combination to make this correction possible. It enables the machine to be used accurately at lower loads than would otherwise be possible. The calibration curves are not straight lines, but for higher loads they become so nearly straight lines that for all practical purposes they can be considered so.

The machine was calibrated for loads upon its straining clevis ranging from 2 to 1500 pounds. The factors limiting the maximum and minimum loads for which each lever combination was calibrated were, respectively: (*a*) time in which rupture could be expected,[1] and (*b*) the degree of accuracy obtained at small loads. Upon the same basis load limits have been recommended for each lever combination and are described in Table II. Since for high loads the calibration curve is practically straight, conversion factors (Table III) may be employed to calculate the load when the recommended limits are somewhat exceeded. However, these factors cannot be used for loads less than the maximum of the recommended ranges shown in Table III. A slight variation in the weight of shot corresponding to a definite load upon the calibrating scale was observed, but in most cases this weight was a negligible percentage of the whole, as noted in Table IV. These results apply to the apparatus under consideration only; however, they are given here to show the accuracy which is attainable with a machine of this design.

TABLE I
LEVER COMBINATIONS

Lever combination	[2] Position of Connecting member	Pulling clevis	Average multiplying power	Suitable for loads from	Suitable rate of flow of shot, lbs./min.
A	*w*	*y*	7.91:1	0 to 25 lbs.	2.25
B	*x*	*y*	15.15:1	25 to 50 lbs.	4.5
B	*x*	*y*	15.15:1	50 to 150 lbs.	9.0
C	*w*	*z*	51.40:1	150 to 400 lbs.	9.0
D	*x*	*z*	99.15:1	400 to 1500 lbs.	9.0

TABLE II
RECOMMENDED LOAD LIMITS, LEVERAGE COMBINATIONS AND RATES OF FLOW OF SHOT

Load at straining clevis (in lbs.)	Leverage combination	Rate of flow of shot (in lbs. per min.)
0 to 25	*A*	2.25
25 to 50	*B*	4.50
50 to 150	*B*	9.00
150 to 450	*C*	9.00
450 to 1500	*D*	9.00

---

[1] The load limits recommended for each lever combination are intended to be such that test specimens will rupture in not more than $1^1/_2$ minutes.

[2] Refer to Fig. 2.

TABLE III

CONVERSION FACTORS

(Weight of shot × factor = load at straining clevis)

Leverage, combination	Shot flowed from bucket	Conversion factor
A	More than 3.3 lbs.	7.91
B[1]	More than 3.3 lbs.	15.14
B[2]	More than 13.0 lbs.	15.61
C	More than 9.0 lbs.	51.35

TABLE IV

OBSERVED VARIATIONS IN WEIGHT OF SHOT CORRESPONDING TO A GIVEN LOAD UPON THE STRAINING CLEVIS

Combination *A*			Combination *C*		
Load at straining clevis, lbs.	Variation from average Maximum %	Av. %	Load at straining clevis, lbs.	Variation from average Maximum %	Av. %
2	5.72	5.72	100	1.47	0.50
10	2.32	1.16	200	0.38	0.38
20	1.18	0.59	400	0.19	0.10
Combination *B*					
30	1.50	0.75			
40	1.13	0.57			
70	0.65	0.33			

TABLE V

LAG

Pounds shot flowed from bucket	Load at straining clevis, Combination *A*, lbs.	Overloading caused by lag, for flow of 9.00 lbs./min., %	 2.25 lbs./min., %
0.390	3.12	21.0	5.4
0.780	6.24	7.0	1.8
1.125	9.00	3.6	0.9
1.530	12.30	1.8	0.5

TABLE VI

VITREOUS BODIES DRIED AT 100°C

(Bars approximately 1″ x 1″ x 6″; span = 5 in.)

Body no.	Lbs. shot	Load at straining clevis (in lbs.)	Modulus of rupture (lbs./sq in.)	Average, lbs.
	2.37	18.6	164	
V_3	1.67	13.0	108	
	2.45	19.4	166	139
	1.59	12.4	109	
	1.92	15.0	162	
	2.16	16.0	127	
	1.98	14.7	123	
	1.76	13.8	118	
V_4	1.74	13.7	122	121
	1.77	14.0	119	

---

[1] Rate of flow of shot = 4.5 lbs. per min.

[2] Rate of flow of shot = 9.0 lbs. per min.

TABLE VI (*Continued*)

Body no.	Lbs. shot	Load at straining clevis (in lbs.)	Modulus of rupture (lbs./sq in.)	Average, lbs.
V_5	1.69	13.3	119	122
	1.77	14.0	126	
	1.62	12.7	105	
	1.91	15.0	126	
	1.92	15.1	134	
SEMI-VITREOUS BODIES DRIED AT 100°C				
SV_2	2.78	21.9	190	178
	1.88	14.7	144	
	2.31	18.2	154	
	3.01	23.9	201	
	2.64	20.9	186	
	2.92	23.2	195	
SV_3	2.41	19.0	186	182
	2.49	19.6	174	
	4.38	34.5	196	
	4.00	32.0	181	
	2.23	17.3	171	
SV_5	2.40	18.9	160	172
	2.61	20.5	190	
	2.43	19.2	163	
	2.48	19.5	165	
	2.60	20.5	169	
	2.75	21.8	185	

TABLE VII

TERRA COTTA BODY FIRED TO CONE 8

(Bars approximately 1″ x 1″ x 6″; span = 5 in.)

Lbs. of shot	Load at straining clevis (in lbs.)	Modulus of rupture (lbs./sq. in.)	Lbs. of shot	Load at straining clevis (in lbs.)	Modulus of rupture (lbs./sq. in.)
10.40	167	1415	3.66	186	1656
10.67	170	1570	3.81	193	1662
8.70	139	1208	2.73	134	1127
12.00	191	1606	3.08	155	1303
10.23	164	1425	3.63	184	1516
11.52	186	1656	4.35	221	1654
9.49	152	1355	3.30	166	1345
9.75	156	1355	3.48	176	1492
	Av.	1449[1]	3.30	177	1539
			3.42	173	1455
			3.57	182	1455
			3.30	177	1539
			3.83	194	1684
			3.86	196	1704
				Av.	1513[2]

---

[1] Leverage combination *B*.

[2] Leverage combination *C*.

While it is recommended that the leverage combination be used which is best adapted to the load required by specimens under test, the data in this table indicate that results are not greatly affected by using another combination.

TABLE VIII
FIRE BRICK
(Approximately 1½″ x 2½″ x 9″)

Span = 5 in.			Span = 8 in.		
Lbs. of shot	Load at straining clevis (in lbs.)	Modulus of rupture (lbs. / sq. in.)	Lbs. of shot	Load at straining clevis (in lbs.)	Modulus of rupture (lbs. / sq. in.
4.96	484	1027	8.18	801	2205
10.88	1066	1854	5.40	528	1187
9.68	1046	1517	5.10	498	911
6.07	594	674	6.08	595	1552
7.88	772	1118	6.45	631	1157
8.56	839	1329	4.95	483	1382
9.53	912	765		Av.	1399
	Av.	1183			

The longer span used in this series of tests shows a higher average result and is probably due to the specimens breaking more consistently at the center.

TABLE IX
GLASS SPECIMENS (ONE SIDE SMOOTH)
(Approximately 2″ x 0.2″ x 20 ″; span = 16 ″)

Type of specimen	Lbs. of shot	Load at straining clevis (in lbs.)	Modulus of rupture (lbs./sq. in.)	Deflection at time of rupture (in inches)
Rough on one side	2.76	21.80	5345	0.102
	2.37	18.34	4782	.103
	2.70	21.30	5635	.109
	2.10	16.45	4270	.095
	2.63	20.69	5652	.117
	2.35	18.50	4932	.103
Rough on one side Wire reinforcement	5.06	39.50	7005	.123
	3.12	24.66	3855	.059
	3.60	28.50	4985	.081
	3.48	27.64	5490	.104
	3.95	31.60	5925	.104
	6.27	49.00	7280	.119
One side corrugated	1.55	17.15	3664	.125
	4.44	34.70	4960	.074
	8.58	67.00	4700	.058
	8.82	68.90	5380	.065
	1.43	11.10	5010	.150
	1.31	10.13	4635	.127

Lag

At loads from 0 to 20 pounds (at the straining clevis) the interval of time between failure of a specimen and cessation of the shot flow becomes appreciable. The effect of this lag may be offset by reducing the rate of flow of shot until the product of the lag and rate of flow becomes a negligible fraction of the total load. The lag at various loads between 0 and 20 lbs. was computed and its effect at two rates of flow is shown in Table V. The large differences found clearly indicate the necessity for applying small loads very slowly.

Results

Tables VI to IX, inclusive, contain results representing the machine's performance.

Other Appliances

The machine is also adapted to determining deflection of specimens under definite loads. The screw to which the pulling clevis is attached was calibrated with an Ames Gage and found to have a pitch of .05 inch. To determine the vertical travel of the screw and clevis the perimeter of the wheel which operates them was graduated in 50 divisions. This graduation furnishes a means of counting the number of revolutions of the wheel required to keep the beam horizontal while loading a specimen and, therefore, a means of determining the deflection of the loaded specimen. To observe deflections under predetermined loads, the flow of shot can be stopped when desired by means of the spring contact *S* (Fig. 4).

TABLE X

CORRECTIONS FOR MACHINE DEFLECTION

Loads (pounds)	Corrections (inches)	Loads (pounds)	Corrections (inches)
0 to 50	0.000	600 to 650	0.013
50 to 100	.002	650 to 700	.014
100 to 150	.005	700 to 750	.015
150 to 200	.006	750 to 800	.016
200 to 250	.007	800 to 900	.016
250 to 300	.008	900 to 1000	.018
300 to 350	.009	1000 to 1100	.020
350 to 400	.009	1100 to 1200	.022
400 to 450	.010	1200 to 1300	.023
450 to 500	.010	1300 to 1400	.025
500 to 550	.011	1400 to 1500	.027
550 to 600	.012		

Deflection in the machine itself becomes appreciable when loads greater than 50 pounds are applied to the straining clevis. Table X, compiled from experimental results, contains corrections which apply within the indicated load limits, and which must be subtracted from the values observed when measuring deflections. No error greater than .002 inch will be introduced by using this table, but each machine must be calibrated individually as the tabulated values refer to this one only.

In order to determine the deflection in the machine, the span was reduced to 3 inches and a steel bar ($1^1/_2$ x 3 x 4 inches) placed across the straining mechanism as a specimen; the bar was loaded at successive intervals of 1.5 lbs. of shot, from 0 to 15 lbs., for each lever combination, and the deflection observed for each load.

Advantages

1. Sensitivity and elimination of the personal element by automatic operation make it possible to obtain accurate results.
2. Adjustment to different spans and lever ratios is easy, and this feature is of importance where a large variety of specimens are to be tested.
3. The simple and rugged construction of the machine insures consistent, dependable service.

THE EFFECT OF HEAT ON THE STRENGTH OF CALCINED KIESELGUHR-PORTLAND CEMENT MIXTURES[1]

BY SAMUEL J. McDOWELL AND HOBART M. KRANER

ABSTRACT

The effect of heat upon the strength of this material is shown. This decreases rapidly at 100°C and remains fairly constant between 200° and 500°C. It decreases until 800° where a slight increase is shown between this and 1000°C. Above this the strength decreases.

Introduction

In certain types of ceramic construction it is highly desirable to use flat slabs which must at least bear their own weight. Very often they are not subjected to extremely high temperatures and a certain amount of heat insulation is desired. For a slab of this kind the monolithic tamped block of calcined kieselguhr grain ("C-3" material sold by the Celite Products Company) and Portland cement suggests itself.

In an endeavor to ascertain the effect of heat on the ability of such a slab to support its own weight or an additional weight, the following experiments were conducted.

Materials

Calcined Kieselguhr or "C-3" Material This was California kieselguhr which had been calcined to 1200°C and in which a volume shrinkage of approximately 25% had taken place due to this firing. The screen analysis of this material as used in these experiments was as follows:

Total residue on	Per cent
4-mesh	0.0
6-mesh	33.3
8-mesh	35.7
12-mesh	47.4
30-mesh	65.2

Portland Cement This was Huron Portland cement made by the Huron Portland Cement Company of Alpena, Mich. Analyses[2] and tests[2] made on the cements used were as follows:

Chem. anal.	
SiO_2	20.30
Al_2O_3	6.04
Fe_2O_3	2.96
CaO	62.50
MgO	2.24
SO_3	1.52

Fineness

17.2% retained on 200-mesh

Setting time	
Initial set	4 hours 40 minutes
Final set	7 hours 30 minutes

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[1] Recd. Aug. 14, 1925.

[2] Made through the courtesy of the Huron Portland Cement Company.

Tensile strength, neat cement	Lbs. per sq. in.
24 hours	400
24 hours	415
7 days	720
7 days	710
7 days	660
28 days	760
28 days	795

Preparation of Test Pieces

A mixture of four parts "C-3" and one part Portland cement by volume is recommended by the Celite Products Company for furnace door backing and foundation construction. This proportion which is the same as 55% "C-3" and 45% Portland cement, by weight, was used.

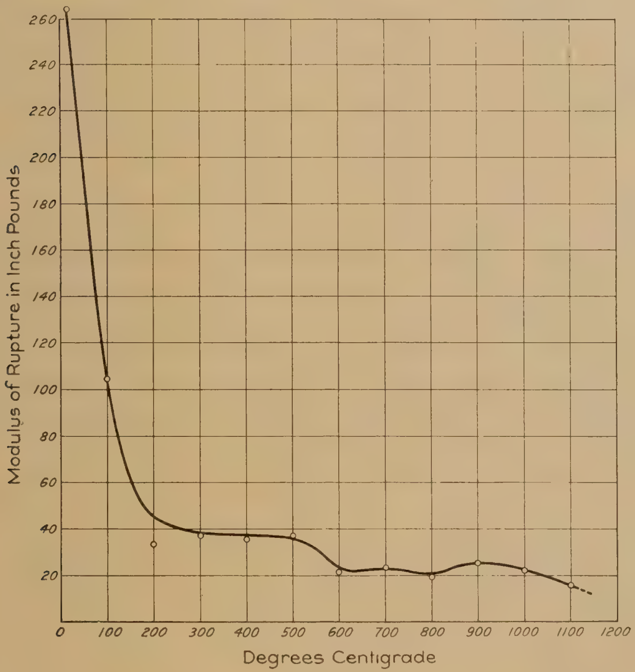

FIG. 1.

The cement and "C-3" material were thoroughly mixed dry by hand. Sixty-five per cent, of this dry weight, of water was then added and the whole again mixed. This gave good tamping or forming consistency which is similar to that used in forming pressed cement blocks.

The damp mixture was pressed by hand into a mold 2 x 2 x 10 inches. The top and bottom of the bars were smoothed with a spatula. They were kept covered with a damp cloth for two days and then allowed to age in air for 28 days.

In order to get an average from as large a number of pieces as possible, and to minimize the differences due to this method of forming, three batches were made up and bars from each followed through separately.

Method of Heating

Two bars from each batch were heated side by side to each temperature in a small electric laboratory nichrome resistance furnace. In order that the heating might be as uniform as possible, the bars were placed in the furnace on three supports instead of being placed on the bottom of the furnace. The temperature was raised at the rate of 100°C per hour until the desired temperature was reached. After being held at this temperature for four hours, the current was shut off and the pieces allowed to cool in the furnace overnight. They were broken each morning immediately upon being taken from the furnace to avoid possible rehydration.

Method of Testing

The bars were broken as 8-inch beams with the load applied at the middle of the span. One-half inch diameter round iron bars were used as supports. The test bars were broken on their sides; that is, the load was applied at right angles to the direction of pressing into the mold when formed. This gave two flat sides parallel with each other made so by the sides of the mold, and which were most suitable as bearing surfaces in testing. Testing on these sides also somewhat minimized the effect of irregularities of structure caused by hand forming.

Results

The modulus of rupture of the bars was determined from the following formula. Results are indicated in inch-pounds.

$$\frac{3Pl}{2bd^2}$$

where P = breaking load in pounds; l = length of span in inches; b = width of bar in inches; d = depth of bar in inches.

	Batch 1		Batch 2		Batch 3			
Temp., °C	Bar A, lbs. to break	Bar B, lbs. to break	Bar A, lbs. to break	Bar B, lbs. to break	Bar A, lbs. to break	Bar B, lbs. to break	Av. lbs. to break	Modulus of rupture
Room temp.	206	222.75	161	145	207	122	177.2	265.8
100	70	82.75	84.25	42	72	lost	70.2	105.3
200	29.9	16	13.25	22	27.5	26.5	22.5	33.8

300	33	27.25	20.25	13.5	24	30.5	24.7	37.1
400	23.75	20.5	20	32	16	30.6	23.8	35.7
500	21	28.5	9.5	5.25	44	40	24.7	37.1
600	17.25	13	8.25	9.4	21.5	15.5	14.2	21.3
700	4.5	13.6	11.5	14.25	33	13	15.0	22.5
800	9.9	8.6	7	10	19.25	20	12.5	18.8
900	19	13.5	13.5	10.75	20	23	16.6	24.9
1000	21.1	20.4	7.75	12.75	7.5	17	14.4	21.6
1100	9.75	14.25	4.5	8.1	23.75	broke in furnace	10.1	15.2

The differences in strengths of the different batches indicate differences in forming conditions although efforts were made to keep the conditions the same.

Figure 1 shows moduli of rupture of these mixtures after heating to the temperatures indicated.

Conclusions

The foregoing results indicate:

(1) Great decrease in strength between room temperature and 100 °C. This might be accounted for by a partial dehydration of the cement at this temperature although S. F. Newberry[1] states that this dehydration starts at 400 °F (204 °C) and is complete at 900 °F (482 °C).

(2) That the strength remains practically constant between 200 °C and 500 °C. The adhesion between the "C-3" and the cement is so great that in these bars heated below 500 °C the fracture is through the "C-3" grains rather than at their surfaces.

(3) A sharp decrease in strength between 500 °C and 600 °C.

(4) That the strength remains practically constant between 600 °C and 900 °C.

(5) That there is a slight increase in strength at 900 °C and 1000 °C This is probably due to initial sintering.

(6) That there is a rapid decrease in strength above 1000 °C. Further sintering or melting around the grains causes a decided change in structure. The light siliceous "C-3" material is dissolved by the glass which is formed at these temperatures. This glass occupies so much smaller volume that the particles no longer have contact and the result is a weak structure.

From the results of these experiments and actual experience with this material in a more practical way, the following are recommended for tamping large monolithic slabs:

(1) Great care should be taken to avoid structural defects so that no planes of weakness develop between the various layers in the tamped

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[1] *Concrete*, May, 1902.

block. Each batch should be tamped as soon as possible after mixing and each layer should be sprinkled slightly with water before a fresh layer is put in.

(2) The use of steel or iron reinforcement is not recommended due to the structural defects which develop and also to the fact that oxidation of the steel bar will disrupt the slab on account of its slightly increased size caused by oxidation.

It is not the desire of the writers to set forth this material as one which will satisfy all conditions, but rather to show that it is effective up to a definite temperature and that it has a decided value in ceramic construction.

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ORIGINAL PAPERS

ANALYSIS OF RECENT MEASUREMENTS OF THE VISCOSITY OF GLASSES.—II[1]

By G. S. Fulcher

ABSTRACT

Viscosity of two series of four component glasses.—The results recently reported by S. English[2] are here analyzed by the method used in a previous paper.[3] (1) *Series* $6SiO_2, 1.2Na_2O, 0.8(CaO+MgO)$. The temperature at which the difference between the viscosity of a glass and the viscosity of $6SiO_2,2Na_2O$ at the same temperature makes a sharp bend is called the aggregation temperature T_A. It seems to correspond to the devitrification temperature. For this series T_A reaches a sharp minimum for the composition $6SiO_2$, $1.15Na_2O$, $0.45MgO$, $0.39CaO$. The viscosity for any temperature also reaches a minimum at or near this composition. (2) *Series* $6SiO_2, 1.1Na_2O, 0.9(CaO+Al_2O_3)$. The curves are similar to those for the first series, T_A reaching a sharp minimum for the composition $6SiO_2$, $1.11Na_2O$, $0.81CaO$, $0.14Al_2O_3$.

Introduction

Since the first paper on this subject was written,[3] English has published his results for two series of four component glasses.[2] The method used in analyzing the data for the three component glasses has now been applied to these later results.

Soda-Lime-Magnesia-Silicate Glasses

The molecular compositions of these glasses are given in Table VIII, taking the total number of molecules as 8 since the glasses are formed by

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[1] Recd. Oct. 5, 1925.

[2] S. English, *Jour. Soc. Glass Tech., Trans.*, 9 [6], 83 (1925).

[3] G. S. Fulcher, *Jour. Amer. Ceram. Soc.*, 8 [6], 339 (1925).

the molecular substitution of MgO for CaO in the glass $6SiO_2$, $1.2Na_2O$, $0.8CaO$—more accurately $6SiO_2$, $1.15Na_2O$, $0.84CaO$.

TABLE VIII

MOLECULAR COMPOSITIONS OF SERIES OF Na_2O-CaO-MgO-SiO_2 GLASSES

Glass number	9	490	491	492A	493	494	331
SiO_2	5.991	5.967	5.942	5.958	6.033	5.978	5.975
Na_2O	1.153	1.148	1.154	1.106	1.117	1.142	1.191
CaO	.802	.644	.548	.463	.324	.265	.012
MgO	.034	.197	.308	.433	.486	.573	.803
Al_2O_3	.020	.044	.048	.040	.040	.042	.019
$SiO_2 + Al_2O_3$	6.011	6.011	5.990	5.998	6.073	6.020	5.994
$CaO + MgO$	.836	.841	.856	.896	.810	.838	.815
Excess ($CaO + MgO$)	− .004	+ .001	+ .016	+ .056	− .030	− .002	− .025
$(SiO_2 + Al_2O_3)/(RO + R_2O)$	3.02	3.02	2.98	3.00	3.15	3.04	3.01

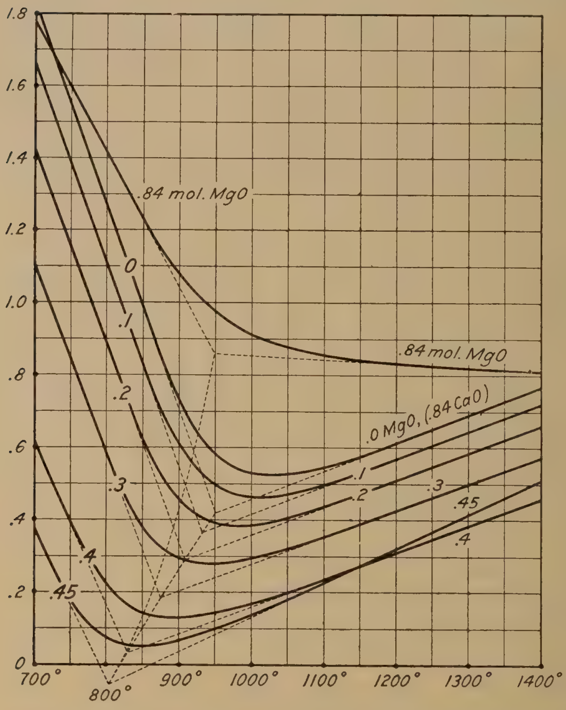

FIG. 17.—$\Delta \log_{10} \eta$ as a function of temperature for a series of glasses $6SiO_2$, $1.15Na_2O$, $0.84(CaO + MgO)$ for 0 to 0.45 molecule MgO, and for 0.84 molecule MgO, as indicated.

From the logarithmic viscosities given by English for these glasses were subtracted the values for the simple trisilicate (glass 1E) for the same temperatures, obtained from a large scale drawing of Fig. 5 (previous article). These differences were plotted as a function of temperature, smooth curves were drawn through the experimental points, and from these the values for certain even temperatures (750°, 800°, etc.), were read. These smoothed results were then corrected for the excess of the amount of ($CaO + MgO$) substituted for Na_2O over 0.84, the assumed corrections per molecule (obtained by plotting change of $\log_{10} \eta$ as a function of CaO for various temperatures, cf. Fig. 6, and determining the slope at 0.84 molecule CaO) being as follows:

Temp.	700°	750°	800°	850°	900°	1000°	1100°	1200°	1400°
Corr./mol.	4.3	4.0	3.7	3.35	2.95	1.75	1.20	1.25	1.40

Correction was also made for the excess of the ratio of (SiO_2 + Al_2O_3) to (Na_2O + CaO + MgO) over 3.00, assuming the following values for the correction per unit difference (obtained from Fig. 2):

Temp.	700°	750°	800°	900°	1000°	1100°	1200°	1400°
Corr./diff.	0.70	0.64	0.60	0.54	0.50	0.46	0.43	0.38

No correction was made for the substitution of Al_2O_3 for SiO_2. Since both excess (CaO + MgO) and excess SiO_2 increase the viscosity, the observed change in $\log_{10}\eta$ is too large in each case, therefore the correction in each case is negative.

The corrected differences for certain constant temperatures were next plotted as a function of MgO content. The values for glass 490 seem about 0.1 too low while those for 491 seem about 0.1 too high to fit in with the other points. Assuming this discrepancy to be due to experimental error (as does English), smooth curves were drawn through the points including values for 0.84 molecule MgO obtained from Fig. 12. From these the values for 0, 0.1, 0.2, etc., molecule MgO were determined. These values, somewhat adjusted to give a consistent family of curves, are plotted in Figs. 17 and 18.

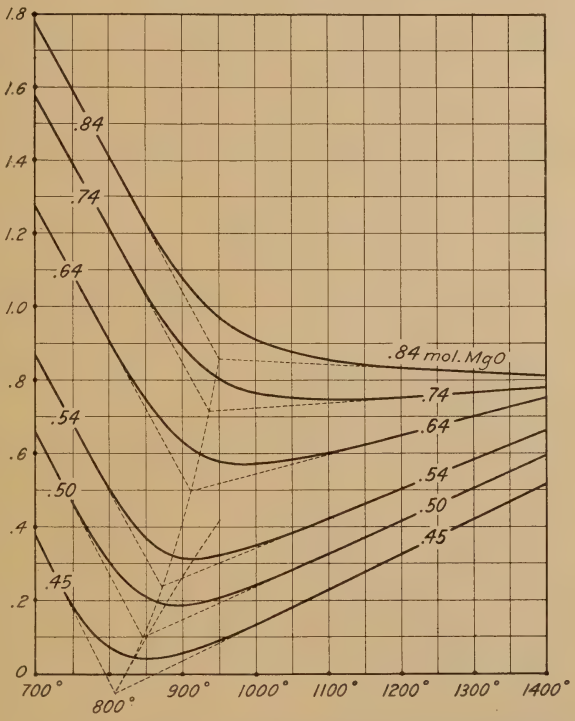

FIG. 18.—$\Delta \log_{10} \eta$ as a function of temperature for a series of glasses $6SiO_2$, $1.15Na_2O$, 0.84(CaO + MgO) for 0.45 to 0.84 molecule MgO, as indicated.

These curves are of the same type as those of Figs. 6, 12 and 14, each consisting of two apparently straight parts joined by a curve. The temperature at which the straight parts (extended) for each curve intersect, will be called, as before, the aggregation temperature T_A for that glass.

The most striking result of the analysis is the way in which this temperature T_A decreases to a sharp minimum (Fig. 19) for a ratio of MgO to CaO of $0.445/(0.84-0.445) = 1.13$, which is very close to the eutectic ratio for the oxides as determined at the Geophysical Laboratory, $1.24 = 0.465/(0.84-0.465)$. This agreement is probably accidental as the eutectic or boundary composition must be between two silicates.

The effect of substituting 0 to 0.45 molecule MgO for CaO in the glass $6SiO_2$, $1.15Na_2O$, $0.84CaO$, is to shift the whole viscosity curve (Fig. 17) to the left and down, decreasing the low temperature slope slightly. The effect of substituting 0 to 0.39 molecule CaO for MgO in the glass $6SiO_2$, $1.15Na_2O$, $0.84MgO$ (Fig. 18), is likewise to shift the curves to the left and down, increasing the high temperature slope considerably and the low temperature slope only slightly. Glasses with about the eutectic compositions have above the temperature of minimum Δ log η (850° to 950°) a less change of viscosity with temperature than the trisilicate $6SiO_2$, $2Na_2O$ with which these glasses are compared, but at lower temperatures the change of viscosity is much greater and intermediate between that due to substitution of $0.84MgO$ and that due to substitution of $0.84CaO$.

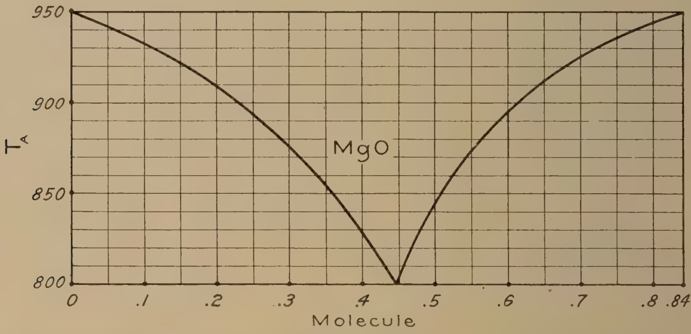

FIG. 19.—Aggregation temperature for $6SiO_2$, $1.15Na_2O$, $0.84(CaO + MgO)$ as a function of MgO content.

Soda-Lime-Alumina-Silicate Glasses

The molecular compositions of these glasses are given in Table IX, taking the total number of molecules as 8 as before, since the glasses are formed by the molecular substitution of Al_2O_3 for CaO in the glass $6SiO_2$, $1.11Na_2O$, $0.95CaO$.

As in the case of the preceding series, the increase of $\log_{10} \eta$ due to the substitution of $(CaO + MgO + Al_2O_3)$ for Na_2O in the trisilicate, was determined for each reading given by English. The smoothed results at

TABLE IX

MOLECULAR COMPOSITIONS OF SERIES OF Na_2O-CaO-Al_2O_3-SiO_2 GLASSES

	10	460	459	458
SiO_2	5.955	5.967	6.048	6.098
Na_2O	1.100	1.056	1.004	.931
CaO	.888	.839	.689	.627
MgO	.036	.011	.018	.000
Al_2O_3	.021	.127	.250	.345
$(CaO + MgO + Al_2O_3)$	.945	.977	.957	.972
Excess $(RO + R_2O_3)$	— .005	+ .027	+ .007	+ .022
$SiO_2/(8-SiO_2)$	2.91	2.93	3.09	3.21

various even temperatures were corrected first for substitution of MgO for CaO using the following values (obtained from Fig. 17):

Temp.	700°	800°	850°	900°	950°	1000°	1100°	1400°
Corr./mol.	1.40	1.40	1.35	0.94	0.40	0.20	0.18	0.18

To correct for excess $(RO + R_2O_3)$ the following values were used (obtained as before from the slopes of $\Delta \log_{10} \eta$ as a function of CaO at 0.95 mol. CaO):

Temp.	700°	750°	800°	850°	900°	950°	1000°	1100°	1400°
Corr./mol.	5.6	5.25	4.9	4.6	4.2	3.3	2.5	1.6	1.7

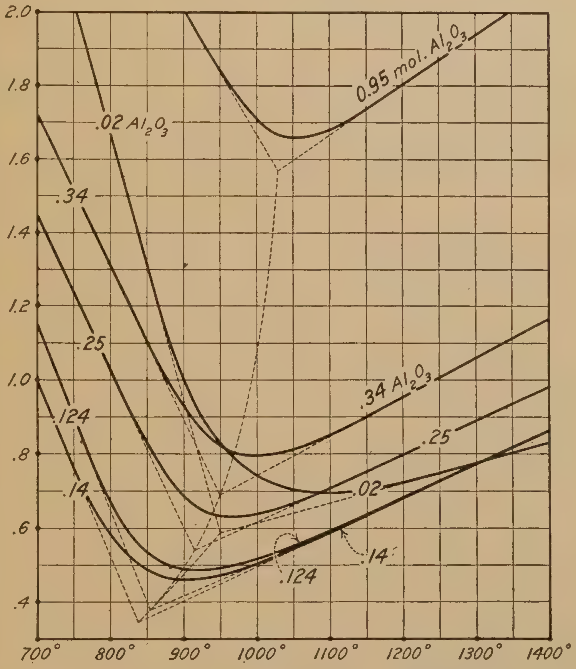

FIG. 20.—$\Delta \log_{10} \eta$ as a function of temperature for a series of glasses $6SiO_2$, $1.11Na_2O$, $0.95(CaO + Al_2O_3)$ containing various molecular amounts of Al_2O_3, as indicated.

Correction was also made for the excess of the SiO_2 ratio over 2.91.

The corrected values for certain temperatures were plotted as a function of Al_2O_3 content and the smoothed values were plotted as a function of temperature. Fig. 20 gives the results somewhat adjusted to give a consistent family of curves. The values for 0.95 molecule Al_2O_3 were obtained from Fig. 13 by extrapolation. The set of curves obtained is quite similar to the set for substitution of MgO for CaO. The aggregation temperature

(Fig. 21) decreases to a sharp minimum which seems to be for 0.14 molecule Al_2O_3 although this is somewhat uncertain because only four glasses were studied. This composition must correspond to a eutectic between two silicates. There is no eutectic between Al_2O_3 and CaO in this region.

The effect of substituting 0 to 0.14 molecule Al_2O_3 for CaO in the glass $6SiO_2$, $1.11Na_2O$, 0.95CaO, is to shift the viscosity curve (Fig. 20) to the left and down, increasing the high temperature slope and decreasing the low temperature slope considerably. The effect of substituting 0 to 0.81 molecule CaO for Al_2O_3 in the glass $6SiO_2$, $1.11Na_2O$, $0.95Al_2O_3$, is also to shift the viscosity curve (Fig. 20) to the left and down, decreasing the high temperature slope and increasing the low temperature slope slightly.

The easiest way to obtain the viscosity curve for any composition intermediate between those for which curves are given in Figs. 17, 18 or 20 is to determine the aggregation temperature from Figs. 19 or 21, locate this on the dotted aggregation temperature curve of Figs. 17, 18 or 20, then draw the high and low temperature lines with slopes intermediate between the two nearest curves and connect them with a curve. To get more accurate results it is necessary to plot $\Delta \log_{10} \eta$ as a function of CaO or Al_2O_3 for various constant temperatures.

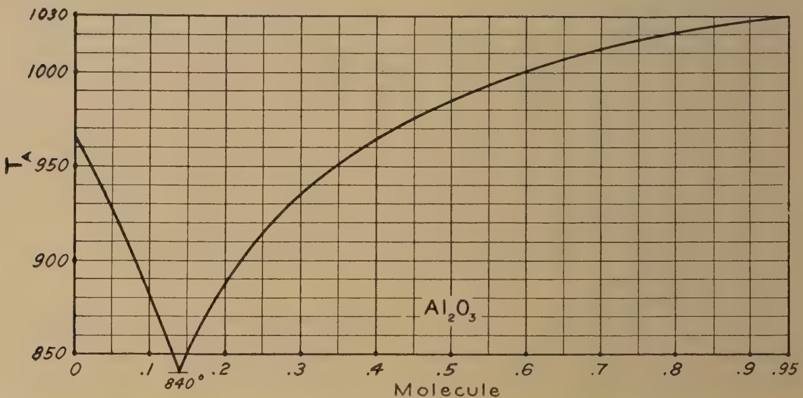

FIG. 21.—Aggregation temperature of $6SiO_2$, $1.11Na_2O$, $0.95(CaO + Al_2O_3)$ as a function of Al_2O_3 content.

The absolute values given in Figs. 17, 18 and 20 may be in error by 0.1 or even 0.2 but the variation of the curves with composition probably corresponds, at least qualitatively, with that indicated by the figures. It would be of interest to determine by quenching experiments whether the compositions $6SiO_2$, $1.15Na_2O$, 0.45MgO, 0.39CaO and $6SiO_2$, $1.11Na_2O$, 0.81CaO, $0.14Al_2O_3$ actually do correspond to eutectics.

CORNING GLASS WORKS
CORNING, N. Y.

A METHOD FOR TESTING THE CROSS-BENDING STRENGTH OF ENAMELS[1]

By R. R. Danielson and W. C. Lindemann

ABSTRACT

Methods which have been proposed for measuring the strength of enamels, by means of impact tests, are not entirely applicable to enameled flat ware, where the ordinary strains are due to bending of the sheets. An apparatus has been devised by means of which bending stresses can be applied in gradually increasing increments so that the normal behavior of enamels under such stresses can be observed and measured.

Introduction

The subject of strength of vitreous enamels is always one of extreme interest and several methods for determining the strength have been proposed. A method for testing the resistance of kitchen ware enamels to impact has been described by Landrum[2] in which a five-pound weight is dropped a distance of $20^1/_4$ inches onto the ware. Various modifications of the impact test have also been suggested by Orton[3] and by Danielson and Sweely.[4]

It will be noted that all these methods are concerned with the resistance of enamels to impact and this is natural since the type of ware to which these tests have been mainly applied usually fail because of stresses received in impact. Such articles, however, as signs and stove parts in the form of flat sheets, probably fail in most cases because of the excessive flexing of the sheets during handling. This type of failure is, therefore, of interest to manufacturers of this class of ware because of breakage encountered at times in the assembling and mounting of enameled parts, and also because of the natural desire to produce ware which will be as free as possible from any inherent tendencies of this sort. How to determine quantitatively, and in a reasonable length of time, what type of enamel or shop practice will give the most satisfactory results in this connection has been a real problem. Bending tests have been suggested but no practical method for applying the load or measuring the flexion has previously been brought forward.

Description of Apparatus

The apparatus shown in Figs. 1, 2 and 3 has recently been constructed for testing the bending strength of porcelain enamels. A transverse load

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, February, 1925. (Enamel Division.) Received Sept. 24, 1925.

[2] R. D. Landrum, "A Comparison of Ten White Enamels for Sheet Steel," *Trans. Amer. Ceram. Soc.*, **14**, 489 (1912).

[3] E. Orton, Jr., "Testing of Enameled Sheet Steel Wares," *Trans. Amer. Ceram. Soc.*, **11**, 320 (1909).

[4] R. R. Danielson and B. T. Sweely, "Relations between Compositions and Properties of Enamels for Sheet Steel," *Jour. Amer. Ceram. Soc.*, **6** [10], 1011 (1923).

is applied to enameled test plates, 2 x 12 inches and of 22 gage sheet steel. In order to eliminate variations in results due to varying thickness of enamel coating, the test plates are weighed after each coat is applied and fired and only those of a specified weight are used.

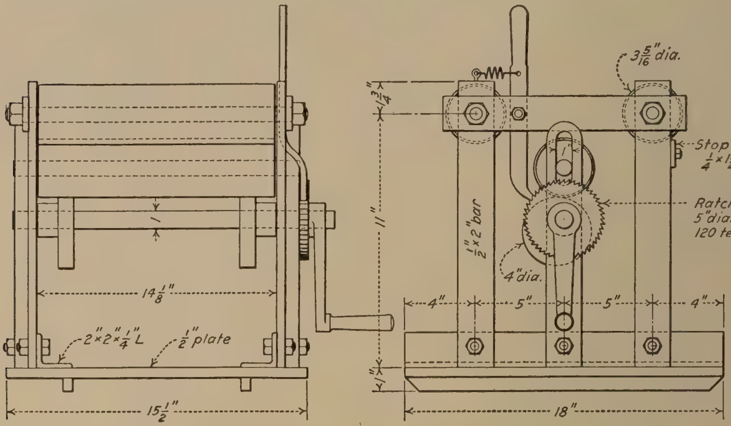

FIG. 1.—Sketch of apparatus for cross-bending tests.

As will be noted in Fig. 3, the test plates are placed against stationary bearing supports made from 3-inch pipe, the load being applied by a movable 3-inch roller fulcrum, which is raised vertically by an eccentric arrangement operated from a ratchet wheel. The 3-inch circular bearing supports prevent sharp bends and also allow for continual readjustment of the bearing points. The two stationary supports are fixed at 10 inches, center to center, with the movable roller halfway between these points. The enameled plates are placed face side up in contact with the fixed supports and the movable roller is raised until in contact with the under side of the plate. Then, by means of the ratchet, the movable roller is raised the desired distance, each notch on the ratchet giving a vertical rise of about $^3/_{64}$ inch. This arrangement places the upper enameled surface in tension and also permits of ready observation of progress of failure during the period of test.

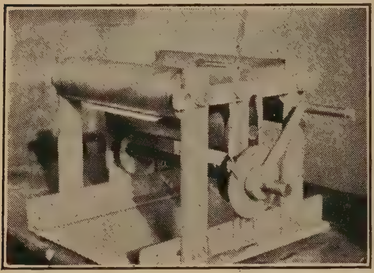

FIG. 2.—View of apparatus showing device for raising movable roller.

In our tests it has been found advisable to make three notches on the ratchet, the initial elevation of the movable roller, and one notch each interval thereafter. These adjustments are made twice each day and observations are made at each interval for the first appearance of crazing or cracking of the enamel, as well as the point at which the enamel flakes from the plate.

TABLE I

RESULTS OF TESTS ON FOUR WHITE ENAMELS

			Condition of Enamels			
Date	Hour when observed	No. of notches raised	Enamel 1, 31.39% feldspar, 8.86% quartz	Enamel 2, 31.39% feldspar, 10.86% quartz	Enamel 3, 29% feldspar, 12% quartz	Enamel 4, 25% feldspar, 16% quartz
1/8/25	5:30 P.M.	3	Good	Good	Good	Good
1/9/25	8:00 A.M.	.	Good	Good	Good	Good
1/9/25	8:00 A.M.	1	Good	Good	Good	Short fine crack
1/9/25	5:30 P.M.	.	Good	Good	Good	Crack lengthened
1/9/25	5:30 P.M.	1	Good	Good	Good	Crack lengthened
1/10/25	8:00 A.M.	.	Good	Good	Good	Crack across plate
1/10/25	8:00 A.M.	1	Good	Good	Good	Crack across plate
1/10/25	12:30 P.M.	.	Good	Good	Good	Enamel flaked
1/10/25	12:30 P.M.	1	Fine crack	Good	Good	Enamel flaked
1/12/25	8:00 A.M.	.	Crack across plate	Fine crack	Good	Enamel flaked
1/12/25	8:00 A.M.	1	Enamel flaked	Enamel flaked	Good	Enamel flaked
1/12/25	5:30 P.M.	.	Enamel flaked	Enamel flaked	Good	Enamel flaked
1/12/25	5:30 P.M.	1	Enamel flaked	Enamel flaked	Fine crack	Enamel flaked
1/13/25	8:00 A.M.	.	Enamel flaked	Enamel flaked	Several fine cracks	Enamel flaked
1/13/25	8:00 A.M.	1	Enamel flaked	Enamel flaked	Cracks enlarged	Enamel flaked
1/13/25	5:30 P.M.	.	Enamel flaked	Enamel flaked	Additional cracks	Enamel flaked
1/13/25	5:30 P.M.	1	Enamel flaked	Enamel flaked	Additional cracks	Enamel flaked
1/14/25	8:00 A.M.	.	Enamel flaked	Enamel flaked	Additional cracks	Enamel flaked
1/14/25	8:00 A.M.	1	Enamel flaked	Enamel flaked	Enamel flaked	Enamel flaked

Colored ink, rubbed lightly into the enamel surface, brings out very definitely the first indications of crazing which are not readily apparent.

Results of Tests

Typical results obtained with this apparatus are shown in Table I. Four white enamels in which the only changes are in the feldspar and quartz content, as shown, have been applied to ground coated plates and subjected to test. It will be noted that the initial failure occurred in the bending of the plates with readings of from 4 to 9 notches on the machine equivalent to a spring in the plates of from $^3/_{16}$ to $^7/_{16}$ inch. This undoubtedly gives a satisfactory range for the differentiation of the enamels, although the results given in this form are not nearly as expressive of the value of the test as that shown in Table I, or even better than this, actual observations of the enamel during the life of the test.

These data have been checked with very satisfactory consistency in the results, and it is quite evident that the machine is sufficiently sensitive to measure cross-breaking strength with the required differentiation for all practical purposes. Sufficient data are not available at this time from which to draw general conclusions as to the effect of replacements of feldspar by quartz and the results are offered merely as indicative of what may be expected in the use of the apparatus. It is only necessary to state that the apparatus has been used successfully for several months to permit of the collection of accurate information on the cross-bending strength of enamels produced under factory conditions.

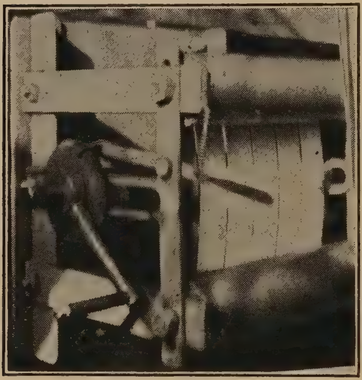

FIG. 3.—View of apparatus showing arrangement of test plates.

Summary

Impact tests which are valuable in indicating the resistance of enamel kitchen ware and similar articles to ordinary abuse encountered in that type of ware, are not satisfactory for determining the ability of enamel flat ware to withstand stresses set up in its handling and use. The apparatus and the method described above apparently serve very well for the latter purpose, and offer a means for quantitatively determining this property.

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THE THERMAL EXPANSION OF REFRACTORIES[1]

By F. H. Norton[2]

ABSTRACT

The thermal expansion or contraction of a number of typical refractories has been measured up to 1700°C in a neutral or slightly oxidizing atmosphere. In nearly every case the expansion curve has been carried to a higher temperature than given by previous data. In a few cases the expansion curve has been obtained for materials that have not been studied in this way before. It is believed that the expansion curve of a brick, if carried to the softening point, gives valuable information as to the performance of that brick in service.

The thermal expansion of refractories has been studied to a considerable extent up to 1000°C, but above this temperature the observations are few and conflicting. As much valuable information can be obtained from the complete expansion curve of a refractory brick, tests were made on a number of typical refractories up to temperatures of 1700°C.

The information that may be obtained from these expansion curves is summarized as follows:

1. The tendency of a brick to spall, other things being equal, is proportional to the coefficient of linear expansion.[3] The coefficient in most cases varies with the temperature so it is necessary to pick out the temperature at which spalling occurs. This has been found by observation to lie between about 300°C where the thermal strains begin to become serious and 700°C where plastic flow[4] is believed to commence in most materials. Usually the maximum coefficient for the whole temperature range lies between these limits, which alone would account for spalling at these temperatures. The non-spalling possibilities of a given material can therefore be judged by the maximum coefficient of expansion between these two temperatures.

2. Nearly all refractories are composed largely of crystals, which may have two or more allotropic forms each of which is stable over a certain temperature range. The inversion of a crystal to another form is usually accompanied by a change in volume which is sharply indicated on the expansion curve. Thus the expansion curve indicates the form and the relative amount of the crystal components. Also in studying new materials the discontinuities in the expansion curve are an aid in studying that material.

3. The total amount of reversible expansion determines the size of the

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[1] Recd. Aug. 10, 1925.

[2] Babcock and Wilcox Fellow, Division of Industrial Coöperation and Research, Massachusetts Institute of Technology.

[3] F. H. Norton, "A General Theory of Spalling," *Jour. Amer. Ceram. Soc.*, **8** [1], 29–39 (1925).

[4] M. C. Booze and S. M. Phelps, "A Study of the Factors Involved in the Spalling of Fire Clay Refractories," *Jour. Amer. Ceram. Soc.*, **8** [6], 361–82 (1925).

expansion joints needed in wall construction. In the construction of crowns a material with a low coefficient of expansion is desirable to prevent pinching the ends of the blocks.

4. The temperature at which irreversible contraction starts is of considerable importance as this temperature is very close to the maximum temperature at which the refractory may be safely used.

Description of Apparatus

A number of preliminary tests indicated that the expansion and contraction of refractory materials was not the same in the reducing atmosphere of the electric furnace and in a neutral or slightly oxidizing atmosphere. It was therefore decided to make these tests in a gas fired furnace with a neutral atmosphere.

The change in length of a specimen was measured by sighting on the ends with filar telescopes. This gave the length of the specimen directly, without the use of some auxiliary member to bring the measuring point outside of the furnace. In all cases specimens one inch square and nine inches long were used. In most cases they were cut out of a standard sized brick, but where the amount of material was limited, as in the case of zircon, the specimen was molded directly to this size. The ends of the specimen were accurately ground before placing in the furnace.

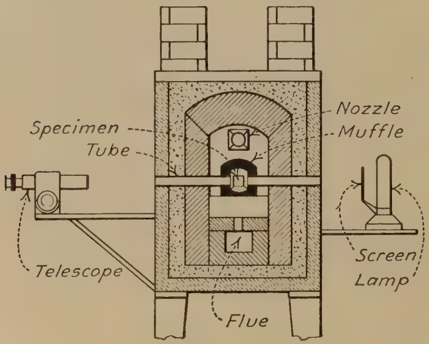

FIG. 1.

A cross-section of the furnace is shown in Fig. 1 and a photograph in Fig. 2. The gas and air from a Maxon premix blower enters under the crown and passes down around the muffle and out through the bottom flue. The muffle was molded in one piece of silicon carbide and four sight tubes were cemented tightly into it. Access to the muffle was gained through the open end.

The telescopes were sighted on the ends of the specimen through the sight tubes and against a bright background produced by lamps with concentrated filaments. This background had an apparent temperature of about 1900°C.

In all runs the temperature was increased at the rate of 100°C per hour. This rate was chosen so that the inside of the specimen would never lag more than 10°C behind the outside. The temperature was measured at low temperature by a calibrated chromel-alumel couple with the tip against the specimen. At 900°C the couple was removed and the temperature read with an optical pyrometer through the sight tubes. The temperature difference between the two ends of the specimens was never more than 10°C and at the higher temperatures was much less.

The highest temperature used in these tests was 1700°C because the specimens either softened or started to react with the muffle and caused fumes. It is believed, from comparison with other furnaces of the same type, that 1850°C could have been reached.

Precision

The thermocouple was calibrated at the boiling point of water, naphthalene and sulphur and at the freezing point of aluminum and copper. The optical pyrometer was calibrated against a Pt, Pt-Rd couple which had been calibrated at the freezing point of aluminum and copper. At the higher temperatures the pyrometer was checked against a standard instrument at the Massachusetts Institute of Technology. It is believed that up to 1350°C the temperatures are correct to ±5°C and above this to ±10°C.

When taking a reading of the length of the specimen the cross hairs on the telescope were set several times and the average taken. Except in a few cases at high temperature where the fluxes in the brick bubbled out of the surface the readings are precise to ±.01% of the length of the specimen. The magnesite and lime specimens reacted considerably at temperatures above 1600°, so the readings above that temperature are erratic.

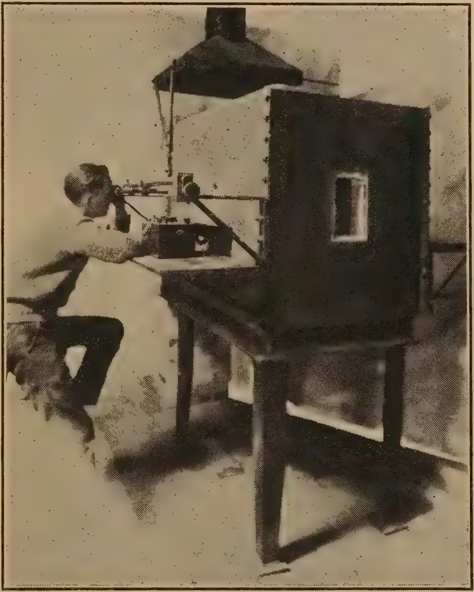

FIG. 2.

Description of Tests

The following list of refractories was selected for test:

1. Silica brick (Pa.)
2. Kaolin brick (fired at 1300°C)
3. Kaolin brick (fired at 1430°C)
4. Kaolin brick (fired at 1500°C)
5. Kaolin brick (fired at 1620°C)
6. Fire clay brick (commercial brick, Mo.)
7. Fire clay brick (commercial brick, Pa.)
8. Fire clay brick (commercial brick, Colo.)

9. Fire clay brick (commercial brick, Md.)
10. Silicon carbide brick (commercial brick)
11. Zircon brick (pure Fla.)
12. Zircon (brown Fla.)
13. Zirconia brick (Brazilian ore)
14. Mullite brick
15. Magnesite brick (pure Grecian)
16. Magnesite brick (commercial brick)
17. Chrome brick (commercial brick)
18. Spinel brick (magnesia spinel)
19. Lime brick (pure commercial lime crystallized)
20. Alumina brick (fused alumina)
21. Insulating brick (commercial brick)

In every case as full a description as possible has been given of the composition and manufacture of the brick or specimen used. It should be noted that in all cases the materials are of commercial purity such as would be used to make brick, and no attempt has been made in the present investigation to study chemically pure refractory substances.

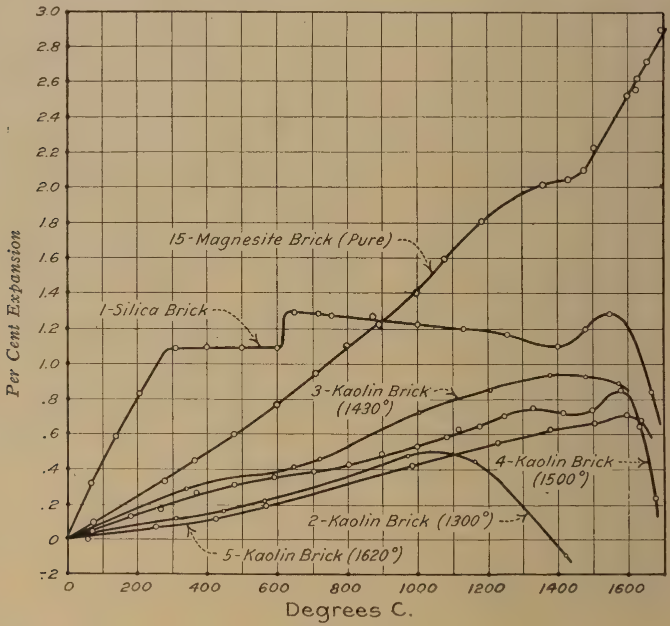

FIG. 3.

The expansion curves for the specimens tested are shown in Figs. 3 to 6. The temperatures in all cases are given in centigrade degrees. The curves are plotted as percentage elongation.

1. Silica Brick (Commercial) The specimen was cut from a standard brick. An analysis of this particular brick was not obtained, but the silica content was probably between 96% and 97%, and according to J. Spotts McDowell[1] contains,

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[1] "A Study of Silica Refractories" Amer. Inst. Min. Eng., *Bull.*, Nov., 1916.

Cristobalite	70%	Tridymite	5%
Quartz	25		

In the same reference are shown expansion curves of quartz, cristobalite and tridymite obtained from various sources.

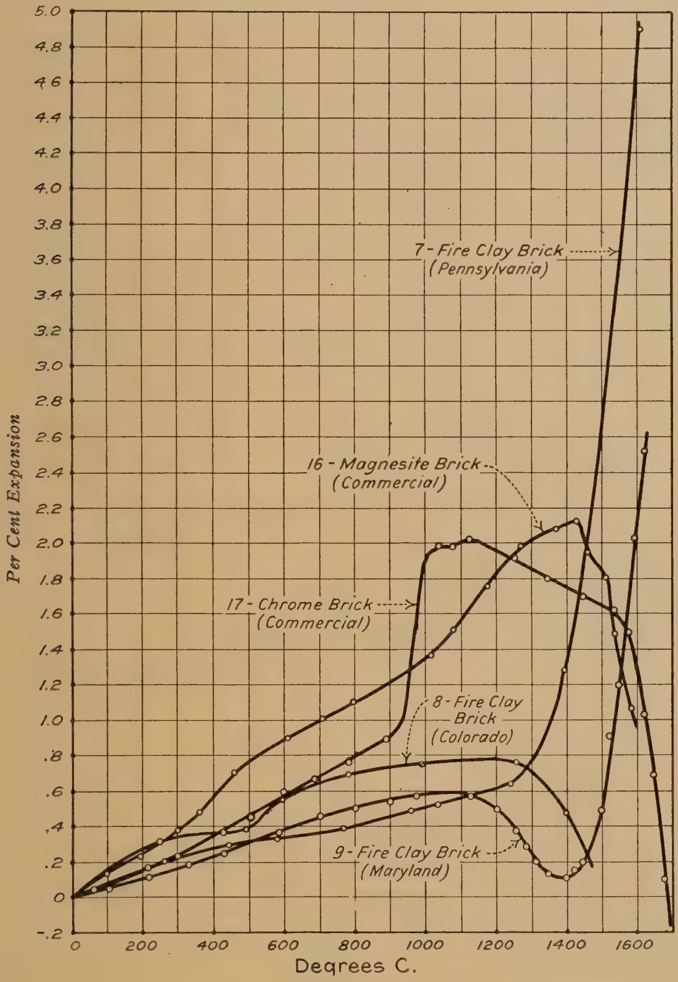

FIG. 4.

The expansion curve for this brick starts up rapidly to 260° where the expansion is 1.09%. The specimen holds this length up to 620° where it suddenly increases to 1.29%. There is no indication of the tridymite inversion point at 110° because of the small amount of this material. The inversion of α to β cristobalite, which is clearly marked at 260°, shows that there is a large porportion of this material in the brick. The quartz inversion point is sharply defined at 610° showing also a considerable amount of this material in the brick.

Beyond 700° the brick contracts slowly to 1400° and then expands rather rapidly to a maximum at 1525°. Above this temperature the brick shrinks quite rapidly and at 1700° starts to soften. The expansion of the brick above 1400° is due to the conversion of tridymite and quartz to cristobalite as the latter material has the lower average density. Fenner gives the formation temperature of cristobalite as 1470°.

It is believed that a high temperature expansion curve of a silica brick will give more information concerning its quality than any other single test.

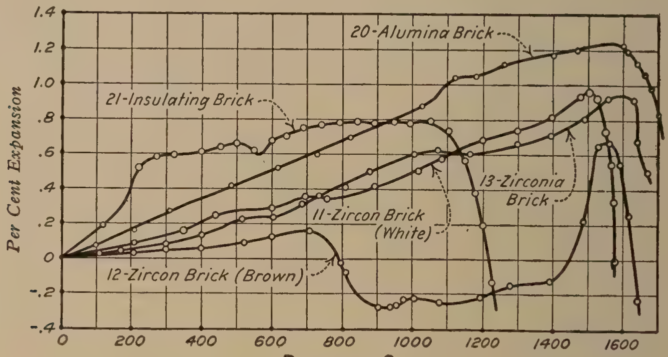

FIG. 5.

2. Kaolin Brick This brick was made of pure kaolin with the following analysis:

Al_2O_3	45.92%	TiO_2	0.35%
SiO_2	52.02	CaO and MgO	none
Fe_2O_3	1.51	Alkalis	trace

The melting point is 1740° (reducing atmosphere).

The grog was fired at approximately 1620° for 30 hours and the brick was fired at 1300°. The structure was soft and crumbly, showing little vitrification of the bond. The porosity was 29.6%.

The specimen shows a steady rate of expansion up to 300°, then it becomes less for the next 200°, and beyond 600° rises more rapidly. The change in slope at 300° corresponds to the inversion of α to β cristobalite, while the increase in slope at 600° corresponds to the inversion of α to β quartz. This portion of the curve indicates the presence of some free silica in the brick in the form of cristobalite and quartz.

The expansion reaches a maximum of .53% at 1075° and then falls steadily as the temperature is increased. This contraction is not reversible and will continue up to the softening point where it amounts to about −6.8%. It is clear that this brick when fired at such a temperature will show excessive shrinkage in use.

3. Kaolin Brick This brick was the same as Specimen 1 except that it was fired at 1430° for 30 hours. The bond had started to vitrify, giving a fairly strong structure. The porosity had decreased to 26.0%.

The expansion curve rises rapidly to 300°, slowly to 600° and then more rapidly to the maximum at 1400°. The free silica in the bond has not combined at this temperature as the transformation points are even more clearly shown than in the lower fired specimen.

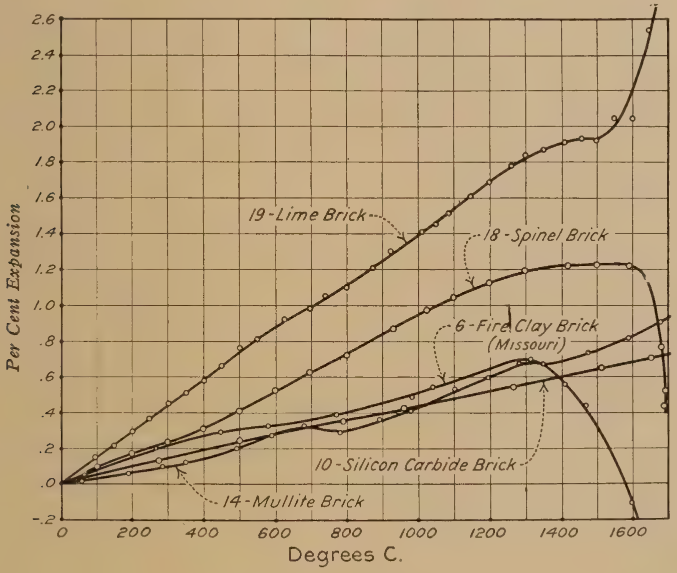

FIG. 6.

The fact that expansion is increased by a higher firing indicates that the bond was vitrified in the second case giving a dense and less porous structure.

The specimen showed a permanent shrinkage above 1400° which increased rapidly above 1600° and amounted to about −6.5% at the softening point.

4. Kaolin Brick This brick was the same as Specimen 1 except that it was fired at 1500° for 30 hours. The brick was harder and more vitrified than the previous specimen, giving a porosity of 24.5%.

The expansion curve rises less rapidly than for Specimen 2 and shows less indication of the silica points. This would indicate that the silica had started to combine with the alumina in the bond to form mullite and silica glass.

The expansion continues up to 1350°, drops off slightly to 1500° and then rises to a maximum at 1570°. This peculiarity in the curve is repeated in the curve for silica brick and must be due to the formation of cristobalite.

The permanent shrinkage is very rapid beyond 1600°C, falling to −6.2% at the softening point.

5. Kaolin Brick

This brick was the same as Specimen 1 except that the firing temperature was 1620° for 30 hours. The specimen was very hard and vitrified with a porosity of 18.0%.

The expansion curve is nearly a straight line with a rather low slope. There is only a very slight trace of the silica points, showing that practically all free silica is converted to either glass or mullite.

The greatest expansion is obtained at 1600°, above which a rapid permanent contraction takes place amounting to −5.2%.

This brick can be used up to 1600° with no permanent change in size, but if the brick is used above 1650° (3000°F) some permanent shrinkage will occur. The performance of the brick in service checks up exactly with these figures.

The tests on this brick at different firing temperatures bring out the fact that the silica content of a fire clay brick is not a measure of the coefficient of expansion as has been sometimes believed, for the firing conditions and form of the silica have a considerable influence.

The curves obtained here are in good agreement with the results obtained at lower temperatures by Houldsworth and Cobb[1] on kaolins fired at different temperatures.

6. Fire Clay Brick (Commercial Missouri)

This is a brick made from a refractory Missouri clay. An analysis of this brand of brick is given as:

SiO_2	53.12%	CaO	0.64%
Al_2O_3	43.30	MgO	0.46
Fe_2O_3	2.48	Alkalis	0.15

The melting point was found to be 1720° (reducing atmosphere).

This specimen expanded fairly steadily up to 1300°, but showed a slight flattening of the curve between 300° and 600° which indicates a small amount of free silica. Above 1320°, which is probably the firing temperature of the brick, shrinkage occurs with increasing rapidity up to the softening point.

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[1] Houldsworth and Cobb, "The Reversible Thermal Expansion of Refractory Materials," *Jour. Amer. Ceram. Soc.*, **6** [5], 645 (1923).

7. Fire Clay Brick (Commercial Pennsylvania)

This is a commercial brick made of Pennsylvania flint and plastic clays. The melting point is 1680° (reducing atmosphere) and the analysis is:

SiO_2	54.16%	TiO_2	2.72%
Fe_2O_3	2.70	CaO	0.10
Al_2O_3	38.84	MgO	1.14
		Sulphates	0.20

The specimen expanded quite evenly up to 1200° with little trace of free silica. Above this temperature the specimen exhibited a peculiarity that is inherent in Pennsylvania clays and in few others. This is the so-called secondary expansion which starts in where most clay brick shrink, and increases rapidly up to 5 or 6% at the softening point.

The theory of this expansion has been discussed but as yet no really satisfactory explanation has been advanced. Two facts, however, are significant: the clay does not show this expansion under load, and a fracture of the expanded material shows a series of bubble-like pores. This leads one to believe that at 1200° some of the fluxes soften and in reacting give off a gas, possibly SO_2 or H_2S, which forms bubbles and increasingly bloats the clay as the temperature goes higher.

At first it might be thought that this property would be a distinct disadvantage in use but when the brick are set in a wall the restraint is sufficient to prevent much of this secondary expansion. A test wall made up of brick of this type of clay not only shows no expansion in length or height when heated to 1600° on the surface for 24 hours, but actually shows a slight shrinkage like other clay brick.

8. Fire Clay Brick (Commercial Colorado)

This is a brick made from a high silica Colorado clay having the following analysis:

SiO_2	62.55%	TiO_2	0.62%
Fe_2O_3	1.13	CaO	0.20
Al_2O_3	35.40	MgO	0.10
		Alkalis	none

The melting point was 1700° (reducing atmosphere).

This specimen expanded very rapidly at first and showed the silica inversion points very strongly, indicating a considerable amount of free silica. A rapid shrinkage took place above 1250°.

9. Fire Clay Brick (Commercial Maryland)

This brick is made from a Maryland flint clay bonded with a similar plastic clay. The analysis of the brick given by the makers is:

Silica	62.32%	Magnesia	0.54%
Alumina	31.65	Alkalis	1.12
Lime	0.10	Titanium oxide	2.30

The melting point is 1610° (reducing atmosphere).

This brick expands up to 1100° rather steadily then starts to shrink rapidly to 1400°. At this temperature the specimen stops shrinking and shows great secondary expansion. This characteristic is rather peculiar, but is due to the same causes as attributed to the Pennsylvania brick. In this case the original firing was so low that actual shrinkage took place before the secondary expansion started.

10. Silicon Carbide Brick (Commercial) This brick is made of pure SiC crystals fritted together at high temperature. No clay bond was used.

The specimen expanded rather rapidly up to 300° after which the slope decreased slightly and remained the same up to the highest temperatures reached. The presence of a very small amount of silica is indicated. On the whole the coefficient of expansion is about the same as kaolin or bauxite and not much lower, as has been sometimes stated.

11. Florida Zircon (ZrO_2-SiO_2, White) This specimen was made from a purified beach sand. It was white in color and was composed of evenly sized particles.

The analysis is as follows:

SiO_2	30.80%	ZrO_2	66.43%
Al_2O_3	1.78	Sulphates	trace
TiO_2	0.50	Undetermined	0.37

It is impossible at present to tell what is the proportion of zircon and zirconia, although the former is supposed to predominate.

The melting point was above 2000° (reducing atmosphere).

The sand was mixed with molasses and fired for two hours at 1650° which gave a firm structure with little vitrification.

The specimen expanded rather slowly to a maximum at 1500° and then shrank rapidly. An inversion point is indicated at 800°, and a slight inflection at 260° and 600°. The latter points indicate some free silica.

12. Florida Zircon (ZrO_2-SiO_2, Brown) This specimen was made from a less purified zircon sand from the same source as the preceding sample. It had the following analysis:

SiO_2	25.00%	TiO_2	9.02%
Al_2O_3	10.50	ZrO_2	55.77

The melting point was 1935° (reducing atmosphere).

The sand was mixed with molasses and molded. It was fired at 1590° for 4 hours.

This specimen showed a low and even expansion at the lower temperatures, but at 800° contracted reversibly nearly one-half a per cent. At 1400° it expanded rapidly to 1550° where it began to shrink.

13. Brazilian Zirconia (ZrO_2)

This brick was made of zirconia ore from Brazil having the following analysis:

Fe_2O_3	1.60%	SiO_2	27.26%
Al_2O_3	7.75	ZrO_2	60.44
CaO	0.04	Undetermined	2.91

The melting point was over 2000° (reducing atmosphere).

The lumps of ore were fired for 4 hours at 1700° which changed their size or appearance very little. The lumps were crushed with difficulty to pass a 4-mesh screen. This was bonded with 20% fine crushed raw ore and 20% molasses solution. The dried brick were fired for 8 hours at 1675° and showed a linear shrinkage of only 2.3% but were slightly distorted. A section of the brick showed that it was well vitrified with a number of bubble-like pores.

The specimen started to expand at a low rate up to 300° and then more rapidly up to 500°. From 500° to 600° it was nearly constant but above this it rose rapidly to 1075° where there was a dip in the curve. This would indicate the presence of some free quartz and some change in the crystal structure at 1100°. Of the silica shown in the analysis, some is free, some combined with the alumina and probably some is in the form of zircon.

The maximum expansion is reached at 1600° above which there is a rapid shrinkage. The expansion curve is very similar to that for the white zircon.

14. Mullite Brick

Biscuits were made up of kaolin and bauxite in such proportions as to make a composition of 72% Al_2O_3 and 28% SiO_2, according to the diagram of Bowen and Greig. The biscuits were fired for 10 hours at 1780° and were converted almost completely to very fine close grained mullite crystals.

The biscuits were crushed to pass a 4-mesh screen, bonded with 30% raw material of the same composition as the biscuit and fired for 4 hours at 1785°. The brick were very hard and vitreous but with numerous pores.

The specimen expanded rather slowly to 700°, contracted slightly up to 800° then expanded steadily up to 1300°. Between 1300° and 1400° the expansion was quite low but increased again up to 1700° where the specimen started to react rather violently with the muffle.

Two inversion points occur, a very distinct one between 700° and 800° and a less definite one between 1300° and 1400°. The first one is probably due to a change of form in the mullite crystals. The second one corresponds with the dip in the silica curve at the same temperature and indicates a slight excess of silica in the brick.

15. Magnesite Brick

This brick was made of pure Grecian magnesite with approximately the following analysis:

SiO_2	3.0%	MgO	89.0%
CaO	2.5	Ignition loss	5.0
Fe_2O_3 and Al_2O_3	0.5		

The melting point was over 2000°.

The calcined material was made into biscuits and fired for 10 hours at 1780° which converted it almost completely into periclase crystals. A very few forsterite crystals were observed.

The biscuits were crushed up to pass a 4-mesh screen and bonded together with 16% of raw magnesite. The brick were then fired at 1680° for 4 hours. They were strong but rather porous and were of a light straw color.

The specimen expanded rapidly and steadily up to 1000° where there was a slight increase in slope. At 1400° there was a small dip in the curve that undoubtedly corresponds to the inversion of the small amount of α periclase in the original brick to β periclase. Above this point the length increased rapidly to a little over 1700° when the fumes caused by the reaction of the specimen and muffle made it impossible to take further readings. The expansion is reversible.

Magnesite is remarkable in having a large and regular expansion which makes the brick rather sensitive to temperature changes and makes large expansion joints necessary.

16. Magnesite Brick (Commercial) This is a commercial magnesite brick which probably contains some iron oxide to bring down the vitrifying point. The brick was dark brown in color and was quite dense.

The expansion curve started up in the same way as the preceding specimen, but at 400° showed an increase in slope due probably to magnesia-iron compounds. This hump in the curve is confirmed by the tests of R. H. H. Pierce[1] on a similar brick. The increase in slope at 1000° is identical with that on the previous specimen. The expansion then continues up to 1440° where it starts to shrink irreversibly to 1680°, after which it shrinks very rapidly beyond the range of the telescopes. This shrinkage is probably due to the change of α to β periclase, which had not been completed in the initial firing.

17. Chrome Brick (Commercial) This is a commercial chrome brick, probably running rather high in iron, but with a high melting point.

This material expands rapidly, with a trace of an inversion point at 600° which indicates a little free quartz. At 1000° there is a tremendous change in size, indicating that some inversion has occurred. This change comes at such a high temperature, however, that it should not cause spalling.

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[1] J. S. McDowell and R. M. Howe, "Magnesite Refractories," *Jour. Amer. Ceram. Soc.*, **3** [3], 227 (1920).

Above 1150° a slow contraction takes place and at 1500° rapid shrinkage starts in.

18. Spinel Brick This brick was made up as follows:

Grecian magnesite was ground intimately with a pure bauxite in the correct proportions to give magnesia spinel. This material was made into biscuits and fired for ten hours at 1730°. The product consisted of about 90% spinel crystals, the remainder being mainly silica and titanium oxide. The biscuits were crushed into grog and bonded with raw bauxite and magnesite in the original proportions. The brick were then fired for four hours at 1690°.

The brick were light colored, composed of many fine crystals and very hard. The melting point was over 2000° (reducing atmosphere).

The specimen expanded fairly uniformly up to 1400°, remained constant to 1600°, then shrank rapidly. There were no indications of inversion points.

19. Lime Brick Pure, calcined lime was heated for four hours at a temperature between 1850° and 1900° in a gas furnace. After cooling, the lumps were hard and composed of glistening crystals. They showed little tendency to slake after one month's exposure in the air.

The lumps were crushed into grog and pressed into specimens without bond. They were fired for one hour at 1740° and gave a firm, hard structure.

The specimen expanded evenly and rapidly to 1500° where an inversion point occurs. Above this temperature the expansion continues rapidly. As this curve is very similar to the magnesite curve it is probable that there is an α and β form of crystallized calcium oxide with an inversion temperature at 1500°.

20. Fused Alumina The fused alumina was in crystals of about 28 mesh size. The analysis showed the material to be quite pure:

Al_2O_3	95.50%	Fe_2O_3	0.44%
TiO_2	3.94	MnO	0.10

The melting point was about 2000°.

The specimen was made without bond and fired at 1650°.

The specimen expanded very evenly up to 1050°, then it expanded rapidly to 1110° and remained nearly stationary up to 1180°. Above this the expansion was regular to 1.23% at 1600°, where irreversible contraction started and reached .70%. Had the specimen been fired harder this contraction would not have taken place.

An inversion point is indicated between 1100° and 1200°.

21. Insulating Brick This is a commercial insulating brick composed mainly of infusorial earth, and has therefore a very low apparent density. The composition is mainly silica. The melting point is 1630° (reducing atmosphere).

The expansion was rapid up to 250° and then very slight up to the shrinkage point at 1050°. A slight dip is evident at 600°, indicating some free quartz.

Discussion of Results

The important characteristics of the specimens tested are assembled in Table I below:

TABLE I

Specimen no.	Type of brick	Melting point (reducing atmos.)	Firing temperature	Mean coeff. × 10^{-7} of expansion between 0°C and shrinking temperature	Max. coeff. × 10^{-7} of expansion between 300°C and 700°C	Max. irreversible contraction or expansion up to 1700°C	Inversion points	Changes in slope	Temperature at which shrinkage or expansion begins
1	Silica	1700°	..	83	1000	1%	260°, 610°	1400°	1550°
2	Kaolin	1740	1300°	47	79	1	260°, 600°	..	1050
3	Kaolin	1740	1430	68	87	1	260°, 600°	..	1380
4	Kaolin	1740	1500	53	70	1	260°, 600°	..	1580
5	Kaolin	1740	1620	43	67	1	....	..	1610
6	Fire Clay (Mo.)	1720	..	54	80	Large	600°	..	1300
7	Fire Clay (Pa.)	1680	..	51	64	—5	600°	1250	1250
8	Fire Clay (Colo.)	1700	..	54	174	Large	260°, 600°	..	1220
9	Fire Clay (Md.)	1610	..	45	80	—3	....	..	1100
10	Silicon Carbide	2000+	..	43	48	0	....	..	1700+
11	Zircon (white)	2000+	1650	64	92	Large	800°	1400	1510
12	Zircon (brown)	1935	1590	42	48	2	600°, 1400°	..	1550
13	Zirconia	2000+	1675	59	87	1	800°, 1150°	..	1600
14	Mullite	1850	1785	53	82	0	780°, 1350°	..	1700+
15	Magnesite (pure)	2000+	1680	142	151	0	1430°	1000	1700+
16	Magnesite (commercial)	....	..	147	210	2	....	500	1440
17	Chrome (commercial)	....	..	104	124	2	1000°	1130	1540
18	Spinel	2000+	1690	76	110	1	....	1200	1600
19	Lime	2000+	1740	138	145	0	1500°	700	1700+
20	Alumina	2000+	1650	77	82	1	1180°	..	1580
21	Insulating	1630	..	74	480	Large	200°, 570°	..	1050

If the specimens are listed in the order of their melting point as in Table II, we obtain an idea of their value for high temperature use.

The first seven specimens may be classed together as very refractory materials for the highest temperature use. The mullite and kaolin belong to an intermediate class, while the silica and fire clay are at the bottom.

TABLE II

Specimen No.	Material	Melting point
15	Magnesite (Grecian)	2000° (pure 2800°)
19	Lime	2000° (pure 2570°)
13	Zirconia	2000° (pure 2550°)
11	Zircon (white)	2000°
18	Spinel	2000°
20	Alumina	2000° (pure 2035°)
10	Silicon Carbide	2000° (decomposes at 2200°)
12	Zircon (brown)	1935°
14	Mullite	1850°
5	Kaolin	1740°
1	Silica	1700°
6, 7, 8, 9	Fire Clay (av.)	1670°
21	Insulating Brick	1630°

It should be emphasized that a high melting point does not necessarily give a high duty refractory, but a high melting point is a primary essential, before other properties can be considered.

In general, the material for a refractory structure should have as small a mean coefficient of expansion as possible. In Table III the various specimens are listed in the order of excellence.

TABLE III

Specimen No.	Material	Mean coefficient of expansion
12	Zircon (brown)	0.0000042
5	Kaolin (hard)	.0000043
10	Silicon Carbide	.0000043
6, 7, 8, 9	Fire Clay (av.)	.0000051
14	Mullite	.0000053
13	Zirconia	.0000059
11	Zircon (white)	.0000064
21	Insulating Brick	.0000074
18	Spinel	.0000076
20	Alumina	.0000077
1	Silica	.0000083
17	Chrome	.0000114
19	Lime	.0000138
15	Magnesite (Grecian)	.0000142
16	Magnesite (commercial)	.0000147

The brown zircon, kaolin and silicon carbide have the lowest coefficients. The fire clay, mullite and zirconia are a little higher, while the spinel, alumina and silica form a still higher group. The chrome, lime and magnesite have values distinctly above the others. Structures made from the last three materials will require carefully designed expansion joints.

As previously stated the ability of a material to resist spalling depends, other things being equal, on the maximum coefficient of expansion between 300° and 700°. In most cases this will be the maximum for the complete temperature range. The different materials are listed below in Table IV to bring out their spalling resistance.

TABLE IV

Specimen No.	Material	Maximum coefficient of expansion between 300° and 700°
12	Zircon (brown)	0.0000048
10	Silicon Carbide	.0000048
5	Kaolin (hard)	.0000067
14	Mullite	.0000082
20	Alumina	.0000082
13	Zirconia	.0000087
11	Zircon (white)	.0000092
6, 7, 8, 9	Fire Clay (av.)	.0000099
18	Spinel	.0000110
17	Chrome	.0000124
19	Lime	.0000145
15	Magnesite (Grecian)	.0000151
16	Magnesite (commercial)	.0000210
21	Insulating Brick	.0000480
1	Silica	.0001000

The materials most resistant to spalling are zircon, silicon carbide and kaolin. Mullite, alumina, zirconia, fire clay and spinel are somewhat less resistant and chrome, lime and magnesite will spall rather easily.

TABLE V

Specimen No.	Material	Temperature at which shrinkage begins
10	Silicon Carbide	1700°+
14	Mullite	1700+
15	Magnesite (Grecian)	1700+
19	Lime	1700+
5	Kaolin (hard)	1610
18	Spinel	1600
13	Zirconia	1600
20	Alumina	1580
1	Silica	1550
12	Zircon (brown)	1550
17	Chrome	1540
11	Zircon (white)	1510
16	Magnesite (commercial)	1440
6, 7, 8, 9	Fire Clay Brick (av.)	1220
21	Insulating Brick	1050

Silica is in a class by itself in regard to spalling. In general this classification agrees well with the behavior of these materials in service.

The temperature at which a material begins to shrink is a good indication of the maximum temperature that it will stand in service. This temperature not only depends on the material but also on its structure and firing temperature, so the values given in Table V do not indicate the possibilities of all the materials.

Silicon carbide, mullite, magnesite and lime show no shrinkage up to 1700° and may therefore be classed as very high duty refractories. Kaolin, spinel, zirconia and alumina shrink around 1600°, while silica, chrome and zircon are somewhat lower. Fire clay brick start to shrink at about 1220°.

Acknowledgments

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METAL POROSIMETER FOR DETERMINING THE PORE VOLUME OF HIGHLY VITRIFIED WARE[1]

By Louis Navias

ABSTRACT

A metal porosimeter of the McLeod-Gage type has been developed for use in determining the porosity of highly vitrified ware. The glass capillary is welded directly on to the 20% chrome-steel metal cap. The metal construction gives a rugged apparatus that can be safely handled for routine work. It is as sensitive as the similar glass apparatus of Washburn and Bunting, but is not structurally delicate. A photograph and drawing with details are included. The suggestion is made that the results obtained by these types of apparatus be expressed as "per cent pore volume," and that the results obtained by water soaking be specifically named "per cent water absorption" to distinguish between them. Results are given to show that for fairly vitrified ware, the water boiling method gives much lower porosity than the method using air as the fluid.

In their study of porosity, Washburn and Bunting[2] developed several types of glass apparatus for the determination of porosity using air or a gas as the fluid medium, in contradistinction to the absorption methods where water, kerosene and vaseline are utilized. For highly vitrified bodies, that is for ware having low porosities, the McLeod-Gage type of porosimeter was recommended.

Such a glass apparatus has been in use in the writer's laboratory for the past year and it has been found to give satisfactory results. There are, however, certain structural weaknesses due to the fact that the apparatus is made of glass. With use the ground glass joint becomes worn, resulting in the cap being sometimes lifted by the mercury, even though it is held in place by extended rubber bands. Care must be taken to prevent sharp impact of the specimen against the glass sides. The specimen has a tendency to remain in close contact with the side of the receptacle when raised by the mercury, and is often retained by the protruding rim of the ground glass joint of the upper half of the apparatus. Sometimes the specimen is dislodged and rises with great force against the glass top, and is liable to do great damage. On account of these facts it was found inadvisable to advocate the use of this precision apparatus by those not particularly familiar with laboratory technique.

Metal Porosimeter

The above-mentioned undesirable features have been eliminated by the construction of a practically all-metal porosimeter. The photograph shows both the glass and metal types, the glass apparatus being assembled while the metal apparatus is unassembled, with the threaded steel collar supported by a clamp merely to show its relative position.

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[1] Recd. Aug. 15, 1925.

[2] *Jour. Amer. Ceram. Soc.*, **5** [8], 528 (1922).

The metal receptacle and cap were made from solid rods of metal, the lower half or receptacle for the test specimens being made of ordinary steel and the upper half or cap being made of steel containing 20% chromium. The inside surfaces are finished as smooth as possible to minimize the entrapping of air when the mercury flows over the surface. The ground glass joint is replaced by a ground metal-to-metal joint having a taper of 45°. For assembling, the two halves are brought in contact, except for the interception of a thin layer of stop-cock grease between the parts of the joint. The collar is threaded into place and if necessary it may be tightened by a spanner wrench. A good vacuum-tight joint is thus easily obtained.

Soft glass can be welded to a tapered chrome steel part and this is the reason for the choice of the special steel. The glass expansion bulb between the metal cap and glass capillary is necessary to enable observation of the rise of the mercury. No effect of the mercury on the metal parts has been noticeable after some months of use.

It will be noted that the glass apparatus has a spherical expansion chamber with a constriction below it to prevent the test piece from rising into it. In the metal apparatus, the expansion chamber is cylindrical having the same diameter as the receptacle. A metal pin welded into the bottom of the cap, acts as an obstruction to the rising test piece, but not to the mercury or gases. By this means the upper half of the apparatus acts as an expansion chamber.

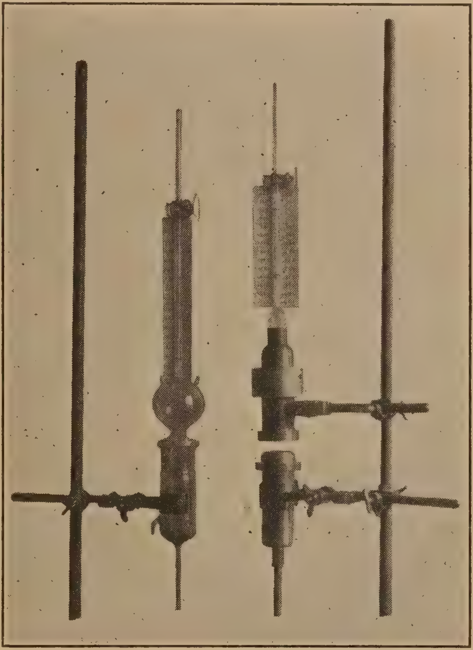

FIG. 1.—Glass and metal porosimeters. McLeod-Gage type.

In both the metal and glass types there are places in the apparatus, especially edges and contacts over which the mercury flows and entraps air. For each apparatus the quantity of entrapped air is a constant. On the photograph it will be seen that the zero mark of the calibrations of the capillary tube begins not at the actual end of the tube at the stopcock but below it. The difference in height (or volume) is the constant referred to, and is determined only once. The glass apparatus illustrated had a constant of 0.11 cc., whereas the glass apparatus of Washburn and Bunting had a constant of 0.14 cc. The metal apparatus has a constant of 0.24 cc.,[1] and requires a slightly longer or larger capillary tube for the same working volume. By more careful workmanship in construction the constant could be diminished.

After the space around the specimen has been displaced with mercury and the stop-cock has been closed, the mercury reservoir is lowered until the specimen reaches the bottom of the receptacle and is surrounded by the gases held in its pores. In the glass apparatus the level of the mercury in the tube below the receptacle is ascertained by visual inspection. With the metal apparatus it is only necessary to determine once the level 76 cm. below the bottom of the receptacle, which must be reached by the leveling bulb to insure the same conditions. The lowering of the mercury and specimen in the metal apparatus causes a vibration which is readily felt by the disengaged hand, and the vibration ceases when the specimen reaches the bottom of the receptacle.

A number of tests have been made determining the pore volume of specimens with both the glass and metal apparatus. In most instances the values obtained were similar, but there were a few anomalous cases, in some of which values with the glass apparatus were consistently higher, while in the others, the values with the metal apparatus were the higher. The cause for the differences was unexplainable.

Effect of Freshly Fractured Surfaces of Ware on Results

It is essential in determining the pore space of a material that at least 50% of the surface be newly fractured. This point is clearly shown by the following examples. Porcelain bars 4 inches long, with a cross-section of 1 square inch, were subjected to test.

		Per cent pore volume	
	Specimen	1	2
(*a*)	One end fractured	0.05	0
(*b*)	Both ends fractured	0.06	0
(*c*)	Same pieces broken through the middle	0.18	0.30

During the molding, finishing and drying processes, the very fine particles of material are brought to and rubbed over the surface, and in the firing process they form a vitreous skin, often more vitreous than the interior of the specimen.

Method of Determination

For the sake of completeness, the procedure for testing is included here as incorporated in the Test Methods of the Engineering Laboratory.

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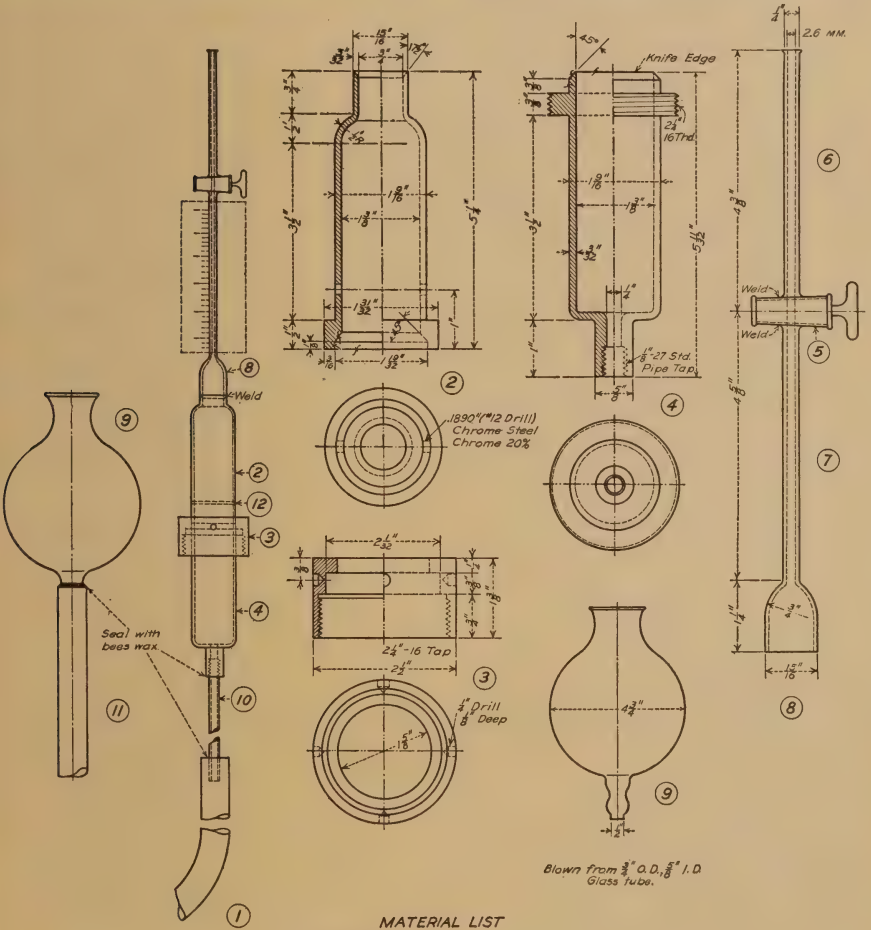
[1] Since the above article has been written another metal porosimeter has been built having a constant of 0.20 cc.

(*a*) After the (fractured) pieces have been assembled in the receptacle of the test instrument and the cap secured in position, the air surrounding the pieces shall be displaced by the mercury by lifting the mercury-leveling bulb. When the mercury level is above the stop-cock, the latter shall be closed. The mercury-leveling bulb shall then be lowered until the lowest surface of the porcelain pieces is entirely exposed. By this means the



MATERIAL LIST
1 - Assembly
2 - Cap
3 - Collar (steel)
4 - Receptacle (steel)
5 - Stop Cock 2 MM. hole (glass)
6 - Tube (glass)
7 - Gauge Tube (glass)
8 - Assembly of Stop Cock and Tubes
9 - Mercury Container (glass)
10 - Pipe 3/8", 12" long, one end threaded (seamless steel tube, iron pipe size)
11 - Hose, 1" O.D., 1/4" I.D., 5'0" (rubber)
12 - Pin, 3/16" × 2 9/16" (steel)

FIG. 2.

gas in the porcelain expands in the outer vacuum, and by a subsequent raising of the leveling bulb the gas is accumulated in the capillary. When the level of the mercury in the leveling bulb and in the capillary are at the same height the gas is at atmospheric pressure, and its volume (V_1) shall be read.

(*b*) The stop-cock shall then be opened and the entire procedure of lowering the mercury level below the specimen, removal of surrounding air, expansion of gas into the surrounding vacuum and accumulation of gas in the capillary, shall be repeated. The second reading of volume (V_2) of gas represents the volume of fine pore space in the specimen. A repetition of the procedure should give a third reading of volume (V_3) similar to the second one. The first value (V_1) is usually too high, since the volume of gas obtained consists of air entrapped on the sides of the porosimeter and held in coarse pockets in the piece of porcelain, and in the fine pores to be measured, and therefore should not be used as a basis for calculation.

(*c*) The total volume (V) of the pieces of each specimen shall be obtained by any suitable volumeter or method, measuring to the nearest 0.2 cc.

(*d*) The pore volume in per cent for each specimen shall be calculated as follows:

$$\text{Per cent pore volume} = \left(\frac{V_2 + V_3}{2}\right)\left(\frac{100}{V}\right)$$

Where V = total volume of test specimen as determined in par. (*c*)

V_2 and V_3 = the second and third volume determinations of gas as determined in par. (*b*).

....

During a run, in case of doubt as to whether the joint is vacuum tight the specimen may be repeatedly subjected to the vacuum and the volume of gas obtained measured after each exposure. If the volume of gas remains the same, then no more gas is being expelled, nor is there a leak. An alternative method is to expel the gas accumulated and then to close the stop-cock and subject the specimen to the vacuum. In this case if there are no leaks, nor gas in the pores, the mercury in the capillary will rise to the contact with the stop-cock.

It is hoped that the types of apparatus employing air as the fluid medium will become more popular, and that their use will be encouraged, and it is suggested that the porosity determined by these means be expressed as "per cent pore volume," signifying the per cent of actual pore space by volume. And where the absorption method is used, that the results be fully described as for instance "per cent water absorption," signifying the per cent of weight of water absorbed by the weight of ware. The relation between the two ways of expressing porosity for porcelain (density 2.38) is given by the equation,

$$\text{Per cent water absorption} \times 2.38 = \text{Per cent pore volume.}$$

"Water Absorption" versus "Pore Volume"

The relative merits of the two methods for determining porosity could properly form subject matter for another paper. However, the following table shows actual values obtained by the two methods.

	Per cent water absorption			Per cent pore volume detd.	
Experimental body no.	4-Hr. boiling	100-Hour immersion. 1 hr. boiling each 24 hours	Per cent pore volume calcd. from 100-hour immersion test	(1)	(2)
190	0.005	0.05	0.12	0.37	0.62
191	.01	.07	.17	.35	.25
192	.005	.07	.17	.66	.52
193	.02	.06	.14	.58	.72
194	.02	.07	.17	.47	.42
195	.01	.06	.14	.46	.20

The identical pieces were used in the 4-hour test as in one of the two determinations for per cent pore volume. It is quite evident that the water absorption method gives much lower results than the method advocated here. There is no doubt that a gas will penetrate into pores which cannot be filled by boiling water in the usual procedure.

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A LABORATORY LOAD FURNACE[1]

By P. D. Helser[2]

ABSTRACT

This paper illustrates the advantages of the laboratory load furnace. The points emphasized are: (1) direct application of load to specimen; (2) perfect alignment of specimen beneath the load; (3) control of temperature ; (4) control of specimen chamber atmosphere; and (5) measurement of volume changes of the specimen throughout the test.

In research work on refractories, a small type of load furnace is very useful for differentiating between the load carrying properties of the various members of a series of bodies. It would be tedious and expensive from the standpoint of time and labor to make full sized brick specimens. It would also be expensive from the standpoint of raw materials, especially if super-refractories were the subject of investigation.

The laboratory load furnace as shown in Fig. 1 is an Ajax-Northrup high frequency induction furnace. It will accommodate specimens from one square inch in cross-section by 2 inches in length to 4 square inches in cross-section by 4 inches in length. Either the standard time-temperature-weight treatment for load tests as specified by the American Society for Testing Materials may be obtained or higher temperatures may be employed, the limit being the refractoriness of the alundum anvils and the specimen chamber walls.

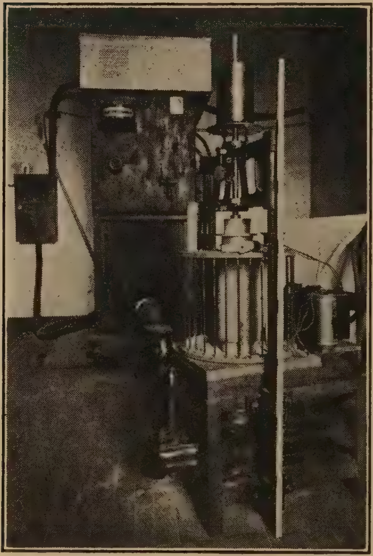

Fig. 1.

The manner of applying the load is rather unique in that the load rides directly on the specimen which in turn is supported on a scale platform, there being no levers or knife edges other than those on the scale itself. After having determined the weight required by carefully measuring the specimen and calculating the total load, sufficient buck shot are added in the hopper to equal this, due allowance being made for the tare weight of the lower anvil and supporting block.

The steel member through which the load is applied is held in a vertical position by means of two adjustable bronze bushings with rounded inner edges which make line contacts with the member, thus minimizing friction. A leveling surface is provided on the member.

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[1] Published by permission of the Director, U. S. Bureau of Mines, Department of Commerce. Recd. Sept. 14, 1925.

[2] Ceramic Engineer, Ceramic Experiment Station, Bureau of Mines.

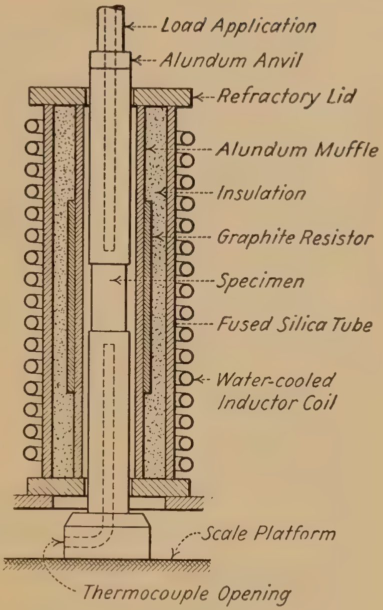

FIG. 2.

The volume changes of the specimen may be closely followed by an Ames dial which is attached to the vertical steel member and to the guide frame.

The temperature may either be measured by an optical pyrometer from above, through an axial hole in the upper anvil or through a similar hole in the lower anvil by a thermocouple. Obviously, the thermocouple may be used above, if the optical pyrometer is not used.

Inasmuch as the furnace is a muffle type, either oxidizing, neutral or reducing conditions may be maintained about the specimen by the introduction of a given gas through a water seal at the bottom of the furnace. If desired, the top may also be sealed similarly.

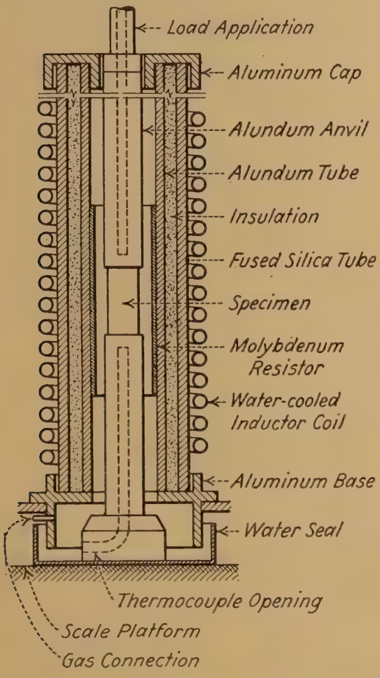

FIG. 3.

A cross-section of the furnace is shown in Fig. 2. The location of the specimen and anvils is clearly shown. The section of graphite resistor is shown immediately without the alundum muffle. A fused silica tube serves as a retaining wall for the insulation which may take the form of calcined magnesia. Lastly the water cooled inductor coils are shown surrounding the furnace proper.

Fig. 3 shows the cross-section of a furnace similar to the above with the exception that the resistor unit is a molybdenum tube instead of graphite. It is located within the specimen chamber in order to favor the alundum tube when the furnace is used for still higher temperatures. It is necessary to maintain either a neutral or reducing atmosphere in the specimen chamber on account of the tendency of the molybdenum tube to oxidize readily. The gas is introduced through the wall of the water seal shown at the bottom of the furnace.

Different types of furnaces such as a carbon resistance, a resistor bar, a gas fired or an oil fired furnace would lend themselves equally well to this load-application equipment.

In summarizing, the following points are worthy of note:

1. Direct application of load to specimen thus minimizing the error due to friction.
2. Perfect alignment of specimen beneath the load thus minimizing the tendency to fail through shear.
3. Control of temperature.
4. Control of specimen chamber atmosphere.
5. Measurement of volume changes of the specimen throughout the test.

Discussion

S. M. PHELPS: How long does the molybdenum tube last in service? We found in the course of some experimental work that the use of this type of tube does not seem to be good practice. How do you weld this material? Is it not possible that the metal of the couples will be heated above the furnace temperature by the eddy currents of induction? Another point is that you measure the compression of the specimen by observing the movement of the rod which applies the pressure; this measurement includes any linear change of the furnace parts.

P. D. HELSER: With regard to the life of the tube, since the furnace has just been built I cannot say how long the tube will last.

As to the welding of the tube, no effort was made to do this. Instead, it was simply rolled into a cylindrical shape and used without being welded.

With regard to the effect of the eddy currents of induction on the reading of the thermocouple no difference was found in the temperature readings. This matter was also taken up with the Ajax-Northrup people and their reply was confirmed by our findings.

With regard to your statement concerning the volume changes of the furnace parts during the test, obviously there would be a thermal expansion of the refractory anvils. Inasmuch as anvils made from the same material were used in each test, the expansion over a given temperature range was considered constant in each test and the results obtained were comparative. It would be possible to obtain absolute values by first running a blank thermal expansion test on the refractory anvils.

L. J. TROSTEL: Is it proposed to have this small load furnace, which will accommodate small test specimens only, replace the larger type of load furnace which will accommodate standard brick specimens? Were the specimens used cut out of standard brick or were they made up in some other manner?

P. D. Helser: It is not proposed to have the small load furnace described replace the larger type of furnace. Instead, the smaller type of load furnace would be especially useful for determining the load carrying properties of a large series of refractory bodies all made up in the same way. Obviously, after the field had been narrowed down to a limited number of bodies which were found to possess good load carrying properties, standard size brick specimens would then be made and tested in the standard larger type of load furnace.

The specimens used were not cut from brick specimens but were made by the dry press process in the size of the specimen tested.

L. J. Trostel: I think a good many of us have found from experience that it is frequently erroneous to consider that the test results obtained on small bars and specially molded pieces are typical of what will happen to the regular run of plant product in the commercial shapes and sizes. This, I believe, would be particularly so in the use of such a load testing machine as Mr. Helser has just described which only tests small cylinders.

It does not seem that data comparable with actual service conditions would result and that primarily is what we are really interested in. Mr. Helser's apparatus strikes me as undoubtedly being an admirable testing device for furnishing comparative data on different ideal specimens but it does not furnish the best approximations to actual service loadings, which, I should say, are only to be achieved by using regular plant run refractories intended for the service the load test simulates, with their usual variations in grind, firing, etc. The present A. S. T. M. load test apparently is better suited to give us this type of information at present.

A LABORATORY KILN FOR OBTAINING HIGH TEMPERATURES[1]

By F. H. Norton[2]

ABSTRACT

A small, gas-fired, laboratory kiln is described capable of firing or melting refractory materials up to 1850°C (cone 38). It is pointed out that the flame temperatures reached approach the theoretical values computed from the heat of combustion and the specific heat of the products of combustion.

The high temperature kiln shown in Figs. 1 and 2 consists of a 24-inch cubical chamber with 9-inch walls. The top of this chamber is covered with a crown supported from the top of the walls. All of the brick exposed to the hot gases are special Babcock and Wilcox brick capable of carrying load at very high temperatures. The joints are made as thin as possible and the inner surface is washed over with cement.

The combustion gases enter the kiln through the back wall by means of a carefully tapered tuyere. This tuyere is just below the crown so that the flame passes over the charge and down to the lateral, bottom flues. The gases are collected by the four stacks at the corners of the kiln and pass out at the top. This stack construction prevents heat loss through the corners of the kiln and allows a close equalization of the temperature by partially closing off the stacks.

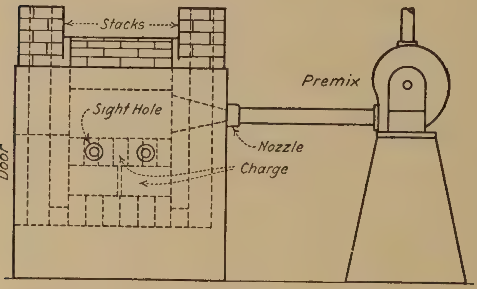

Fig. 1.—Side view of high temperature kiln.

The door is in the front wall and is large enough to give easy access to the interior. The insulation consists of insulating brick $2^1/_2$ inches thick. These are surrounded by a steel shell.

Gas and air are supplied to the kiln by a Maxon Premix blower delivering into a 4-inch pipe. Care was taken to have no bends or restrictions in the line. About 5000 cu. ft. per hour of natural gas are used at the higher temperatures.

The kiln will hold from ten to twenty bricks in a charge, and they are usually set on edge with $^1/_2$-inch spaces between them. The kiln will also hold several large crucibles for making fusions. Care must be used in selecting the setting sand used at high temperatures to prevent sticking.

In Fig. 3 is shown a curve of the temperature rise in this kiln when given the most favorable adjustment. Temperatures of 1850°C have been repeatedly reached and held as long as 10 hours. It is believed that an even higher temperature could be reached but the kiln lining deteriorates rather rapidly above 1800°C. The atmosphere in the kiln can be made oxidizing, neutral or reducing until the higher temperatures are reached, then neutral conditions must be maintained.

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[1] Recd. Aug. 20, 1925.

[2] Babcock & Wilcox Fellow, Division of Coöperation and Research, Massachusetts Institute of Technology.

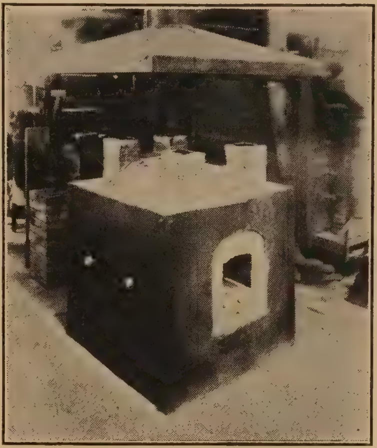

FIG. 2.

The temperatures were measured with a Leeds and Northrup optical pyrometer that was checked against a similar instrument with a Bureau of Standards calibration and against a thermocouple calibrated from the freezing points of pure metals. It is therefore believed that the temperatures are correct within 15°C. The value for the maximum temperature is confirmed by the fact that several times brick with a melting of over 1800°C have flowed freely in the kiln.

It should be noted that the high temperature is attained by the design of the tuyere, combustion space, baffles and flues and not by preheating or heavy insulation. We have constructed a number of furnaces with better insulation, using the same gas and air supply, in which it was impossible to reach over 1700°C.

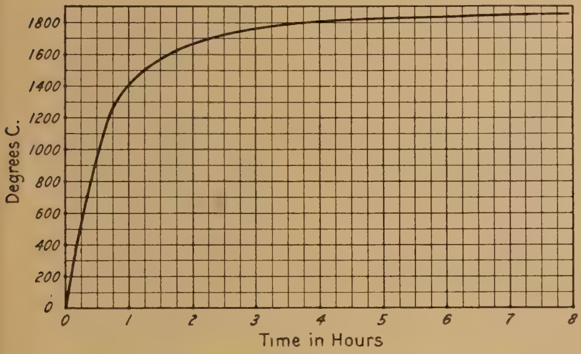

FIG. 3.—Temperature rise in laboratory kiln.

This kiln has been found very useful in the study of refractories, as comparatively large amounts of material such as clays, kaolins and some bauxites can be fused and recrystallized. Materials with higher melting points can be shrunk down to their maximum density. This kiln also gives a large, high temperature field for pyrometer calibration.

While the actual flame temperature reached in this kiln cannot be directly measured, it is estimated from tests at lower temperatures to be at least 50°C higher than the temperature of the walls. This gives a quite conservative figure of 1900°C for the actual flame temperature. This value is nearly as high as the theoretical maximum values for this gas, which works out by the specific heat equations of Lewis and Randall,[1] to be 2075°C when there is no dissociation.

While it is perhaps a little dangerous to predict the upper limit of combustion temperatures, I think it will be quite evident from the present results that we have not yet reached this limit. Let us suppose that we have refractories capable of withstanding the temperatures, and can preheat the incoming gases to 1000°C (the maximum practical temperature) we should have an increase in the flame temperature of about 500°C. This would give furnace temperatures of 2300°C for the natural gas. With fuel oil even higher temperatures might be expected. Such temperatures are sufficient to carry out most of the commercial electric furnace operations, such as fusing alumina and making silicon carbide.

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[1] Lewis and Randall, *Jour. Amer. Chem. Soc.*, **34,** 1128 (1912).

THE MANUFACTURE AND PHYSICAL PROPERTIES OF DRY PRESS BRICK

By J. H. Kruson and C. A. Smith

ABSTRACT

The process of manufacture of dry press brick is described and physical differences between dry press and stiff mud brick are enumerated. The advantages of the dry press process are summed up as follows: (1) they are uniform in size and shape; (2) they have small spalling loss; (3) they have good fusion resistance; (4) their heat conductivity is less than brick made by other processes; and (5) they have a low rate of manufacturing costs.

Introduction

Very few dry press refractory brick were being made twenty-five years ago although one plant in Missouri and two in Ohio have been using this process for at least twenty-five years.

As dry pressing is radically different from hand and machine methods, there naturally has been considerable prejudice and skepticism regarding the value of dry press brick.

The large demand for refractories and the acute shortage of dependable labor, during and after the late war, caused several to produce fire brick by the dry press process and much of the prejudice against them has been removed.

Preparing Clay

Successful manufacture depends largely upon the condition of the clay. There are no set rules for preparing the clay, for each clay and product differs in physical characteristics. The most important factors are: (1) grinding and sizing, (2) moisture content, (3) uniform mixture of clay particles.

Grinding Grinding is usually done in dry pans, and the screening or sizing over a vibrating or shaking type of screen. The inclined slotted plate screen is used in some localities. The proper sizing of the clay particles is an important factor in the making of a good product but this sizing varies with the physical characteristics of the clay.

Characteristics of the Clay

Moisture Content In practically all plants all the water required for pressing is added at the dry pan. The water is thus evenly distributed through the clay. Undoubtedly, this method of adding moisture decreases the grinding and screening capacities considerably.

The moisture needed depends upon the type of clay. Some soft, fine clays require from 9% to 12% of water, while the clays of a flinty nature require from 6% to 9%. Some little variation in weight of individual brick may be expected under ordinary working conditions.

The following table shows weights in ounces of brick directly off the press from three entirely different sources:

TABLE I

Sample	No. 1, oz.	No. 2, oz.	No. 3, oz.
A	149	158	143
B	146	154	144
C	152	162	147
D	150	156	140
E	148	160	142

While there was some little variation in weight, these samples when fired were apparently similar regarding size, ring, bond, appearance, etc. There is no doubt, however, but that a large difference in weight would produce brick which, when fired, would differ in quality.

Sizing of Ground Clay

The following shows a typical screen analysis of hard fire clay used by three Missouri companies:

Mesh	No. 1	No. 2	No. 3
On 4	0.00	0.00	0.00
4–6	0.06	0.00	1.10
6–10	11.70	8.10	16.90
10–14	25.50	21.20	26.20
14–28	27.50	24.50	29.10
28–35	13.30	16.80	9.20
35–48	7.40	11.40	6.10
Through 48	14.10	17.30	11.20
	99.56	99.30	99.80

Pressure

The pressure necessary to form a substantial bond in a pressed brick depends entirely upon the nature of the clay. Many soft, naturally fine clays and shales require little pressure, while a hard flint or a mixture high in non-plastic materials demands an enormous pressure (around 5000–6000 pounds per square inch or more).

Drying

The strength of the unfired pressed brick will permit placement directly into the kiln off the press, whereas all stiff mud brick must be dried before any weight can be placed upon them.

The drying, whether done in the kiln or a drier, is much more delicate than the drying of most mud brick and tile.

Watersmoking

Many dry press brick are watersmoked for six to ten days. This depends entirely upon the physical characteristics of the clay. In general, Missouri fire clays are almost fool-proof if just ordinary care is exercised in the drying and firing. Several manufacturers are setting the brick direct from the press, drying and firing in periodic kilns in from six to seven days and getting excellent results. Others run their brick through driers. However, their firing time and coal consumption is but little different.

Personally, setting the brick directly from the press is preferred. Induced or forced draft is advisable when brick are dried in the kiln.

Firing After the watersmoking is completed, there is but little difference between the general firing procedures for stiff mud and dry press brick from the same clay, other than a temperature of $1^1/_2$ to 2 cones (50–75°F) higher and an additional 12 to 24 hours longer on high fire or soaking period for the dry press. The additional time and temperature naturally consume from 150 to 200 pounds of coal per M brick more than for stiff mud products.

Physical Differences between Dry Press and Stiff Mud Brick

The general differences between brick of similar analysis and clay characteristics from the dry press and stiff mud methods of manufacture may be readily appreciated from the following:

Standard test	Dry press	Stiff mud
Spalling	2.3% per dip	3.5% per dip (as received)
Calculated from total loss and total no. of dips	3.3% per dip	3.6% per dip (on reheating)
Volume change	0.11%	0.21%
Upon reheating at 1400°C	Expansion	Expansion
Slag penetration	1.5 sq. in.	0.60 sq. in.
Load test	1.8% Deformation	2.7% Deformation
Porosity	17.0%	12.5%

The more open or less dense structure of dry press brick is clearly shown by its greater porosity, slag penetration and by its lower spalling loss. The lower volume change of dry press brick upon reheating at 1400°C also shows the lower density of the structure, although it should be pointed out that this test has not been found reliable. The values determined by it do not seem to always hold under actual service conditions in practice and this test is now generally used only as a preparatory step for the spalling test.

The load test shows that the coarser grained dry press brick develops a lesser degree of vitrification than the finer grained stiff mud brick, and that the coarser grains have been firmly pressed together in the manufacturing process, forming a rigid skeleton or framework which resists a steady pressure quite well.

With some clays, the refractoriness of the product may be increased one or two cones by the use of the dry press process, since vitrification does not develop as swiftly in the coarser grained dry press brick as it does in the stiff mud brick.

Advantages of Dry Press

The brick produced by each of the different processes have properties which fit them better for some service conditions than for others. The advantages of dry press brick are several:

(1) Dry press products are always more uniform in size and shape, thus enabling them to be laid up better and with less labor cost, using thinner mortar joints and getting longer life from the installation, due to less tendency for shrinkage and corrosion in joints.

(2) The spalling loss is considerably less than that of brick made by other processes.

(3) Dry press brick resist fusion better than other brick made of same clay, due to slower development of vitrification.

(4) The conduction of heat through dry press brick is less than through brick from other processes, thus reducing the heat loss through the walls.

(5) Dry press brick are cheaper to manufacture, due to lower labor, machinery and drying costs.

Dry press brick are not suitable for service where they will be subjected to severe abrasion, mechanical shock or slag action and greater care must be taken in handling them during manufacture and shipping, due to the sharp edges becoming battered.

Some of the applications of dry press brick are high duty boiler settings, oil refining stills, annealing furnaces (car type), forging and welding furnaces, ceramic kilns (tunnel and periodic), regenerative furnaces (side walls and conducting flues), ladle brick and puddling furnaces (upper side walls).

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OPERATING CONDITIONS IN THE OPEN HEARTH AS THEY AFFECT THE LIFE OF REFRACTORIES

By Charles A. Smith[1]

ABSTRACT

A discussion of the deterioration of refractories under operating conditions of the acid and basic types of open hearth furnaces is given.

Introduction

The object of this paper is not to develop the subject in great detail, but to point out the more salient features of the deterioration of refractories under common operating conditions of the open hearth. The construction of the acid and basic types is practically the same with the exception of the hearth, which must of necessity be acid in the one case, and basic in the other.

Acid Open Hearth

Due to the entire lining of the acid furnace being of the same chemical nature as the slag, which is relatively small in amount, and since no volatile fluxes are added to the charge, the life of the acid furnace is much greater than that of the basic, being frequently 1000 heats. The chief active corrosion of the acid furnace lining results from iron oxides attacking the silica hearth at the edges of the bath where greatest oxidation occurs, and from the scorifying action upon the hearth of molten metal, oxidizing as it is being melted. Steel scrap if charged on the hearth, will attack the hearth greatly in melting due to the large percentage of oxide in the scrap.

Basic Open Hearth

The life of the basic open hearth is much less than that of the acid hearth, being rarely over 350 heats. The relatively shorter life of the basic furnace may be ascribed to the fact that a large part of the lining is of a nature chemically opposite to that of the thin, highly corrosive, basic slag and the furnace atmosphere which is heavily laden with highly basic vapors, flux dust and slag particles.

Ports and Flame Action

The silica roof, the ports, and the checkers, are generally the determining factors in the life of a furnace, and of the three, the ports and the roof are the most troublesome.

While the customary American port design, consisting of a long, narrow air port directly above a much smaller gas port, produces a fast working furnace and allows better combustion without danger of burning the port at the out-going end, the arch forming the gas port is subjected to high temperatures by the gas on one side and the air on the other, thus affording no opportunity for cooling. These conditions produce failure of the nozzle, or end of the gas port, and cause the flame to be thrown upon the walls and roof of the furnace.

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[1] Refractories Fellow, Lehigh University, 1923.

In order to prevent the local overheating and consequent failure of brickwork resulting from this lack of flame control, water-cooled steel ports have been introduced with a fair degree of success. This type of port is of the same general form as the ordinary brick arch port and is inserted through the end of the furnace, being protected by a permanent silica brick arch closely conforming to the outer shape of the metal port.

In some cases the end of the brick arch consists of magnesite brick in order to withstand the action of slag splashes, although magnesite brick spall excessively at this position due to the water cooling.

The ports are so constructed that the flow of gas and air should strike the level bath at a slight angle, and the intensely hot radiant flame should pass through the furnace close to the bath and be separated from the roof by a blanket of cooler air. But during the melting process the furnace is piled high with steel scrap, which forms an excellent baffle from which the flame can be deflected strongly against the roof and side walls. Due to the swirling action given the gases by the incoming air impinging sharply on the top of the gas flow, very hot eddy currents are produced at the side walls opposite the "spotting" point of the flame, if the furnace is slightly narrow. This causes a very heavy corrosive action on the side portion of the roof and lower side walls, in some cases necessitating the building of a roof having a 9-inch center and 12-inch sides in order to prevent the dropping of the entire roof.

Frequently while repairs are being made on parts of the gas producers of a furnace designed to burn producer gas, an oil burner is inserted through a gas port. When a furnace of this type is operated on oil, the life is often reduced about 50% due to the roof being much too low for the intense heat generated by the oil flame. If the roof be raised several feet, a very fast working furnace is produced by oil firing and the flame action is distributed to all parts of the furnace, instead of largely to the roof. The oil-fired furnace has a much shorter life than the gas furnace but the increased production offsets the cost of rebuilding.

Powdered coal has not been found to be desirable as a fuel in a regenerative furnace due to the immense accumulation of ash collecting in, and also fluxing the checkers.[1]

Roof

While the acid nature of the silica roof is entirely unsuited to withstand the fluxing and scouring action of the gas, which is heavily laden with abrading and fluxing particles, silica is used because of its relative cheapness and ability to withstand the excessive temperature, which frequently is in the region of 1700°C. Silica brick are used, due to their property of withstanding the high pressure of the flat-arched roof, up to a point close to the melting temperature. Also the high heat conductivity of the silica brick allows the outer portion to remain firm and rigid even if the inner portion is fused. It is common practice to use a silica roof until it is reduced to about 3 inches in thickness. On examination the iron-impregnated lower portion of a roof brick clearly shows the strong fluxing action of the iron and other basic oxides in the furnace gases.

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[1] R. H. Landis, "Pulverized Coal in Open Hearth Work," *Iron Age*, **112,** 1721–3 (1923).

Side Walls

The silica side walls are subjected to the direct slagging action of the highly corrosive basic slag at or near the slag level in addition to the scouring and fluxing of the gases. The load carried is merely that of the wall itself, due to the weight of the roof being carried by a special steel framework built around the furnace. The brickwork is subjected to considerable thermal shock during charging and after tapping, especially near the doors, which are then wide open and admit large amounts of cold air. Magnesite and chrome have not been very satisfactory for this reason, due to their strong tendency to spall. The direct action of the slag is great, and the lower portion of the side wall from a few inches above the slag line down, is sometimes made of a very high quality chrome brick in preference to several courses of chrome separating a lower portion of magnesite from the upper portion of silica.

In the construction of 200-ton tilting furnaces for the "Talbot" process, the basic lining must necessarily be carried up the side walls for a considerable distance to prevent slag action on the walls during tilting. Frequently, in this type of furnace, the wall on the tapping side is made entirely of magnesite. Since much of the metal is charged molten, and, therefore, quickly charged, and since repairing the bottom takes less time due to the tilting action, the sudden cooling of the brickwork by air currents and the resultant spalling is materially reduced.

Hearth

While the hearth is corroded by the slag, especially at the highly oxidized edges of the bath, it can be and is patched after every melt, and consequently the corrosive action is less important than in other parts of the furnace. The hearth must, however, be highly resistant to abrasion and mechanical shock and must be able to withstand the loads charged upon it. The structure must be dense and firm throughout the range of temperatures used, in order to prevent the absorption of metal and slag, thus lowering its refractoriness.

The formation of cracks resulting from mechanical shock is highly undesirable, since it allows a passage for the metal to work down, and as a result, large sections of the bottom may work loose and allow the molten metal and slag to eat through the steel shell supporting the structure. The chief trouble with the hearth occurs in the formation of holes or depressions which may result from mechanical shock, thermal shock, or improper sintering.

Bulkheads

The bulkheads may be termed that portion of the end of the hearth which extends up to the gas port. The service conditions are different from those of the hearth, the corrosive action of the slag itself being accompanied by the scouring and fluxing action of particles in the exit gases, and there is considerable direct flame action in addition. Material is not charged in this portion of the furnace and therefore the mechanical shock is not important.

Slag Pockets and Uptakes

The uptakes and slag pockets leading from the gas and air ports to the regenerators are generally built of silica brick, even though the gases passing through them carry highly basic particles and flux the brickwork greatly. Magnesite is not used extensively, due to spalling action resulting from the repeated heating and cooling during reversals. However, in some cases, it is used directly back of the ports in the top of the uptakes. The outgoing combustion gases may be at temperatures of 1500–1650°C, while the preheated incoming air and gas, upon reversal, are at from 1000–1100°C at the top of the uptake. Thus, the temperature, abrasion and basic fluxing action are great throughout the uptakes and slag pockets. In addition to the above reactions, the incoming gas in the gas flues is of an extremely reducing character which is of importance in the selection of a suitable refractory.

Regenerators

The regenerators are used not with the primary idea of saving heat, but with the purpose of obtaining a high flame temperature, *i. e.*, a high difference of heat potential between the combustion gases and the furnace charge. The temperatures are such that fire-clay brick can be used for the checkers. The waste gases enter the regenerator at from 1300–1500°C and leave at from 400–600°C. The chief requirements of the brick used as checkers are: that they must absorb and give up heat readily, must not glaze, and in the gas checkers, brick high in iron should not be used, due to the disruptive action of the carbon deposited by the CO in the gas. Although properly designed slag pockets remove a large part of the slag and flux particles from the gases, a considerable amount of dirt collects in the checker flues. Numbers of special flue designs have been tried with varying degrees of success. In a plant in which standard 4.5″ x 4.5″ x 10.5″ brick checkers had to be cleaned after 145 heats, the same chamber filled with $5^1/_2$″ vertical flues using 13.5″ x 6″ x 2.5″ shapes, lasted 1800 heats before cleaning and gave satisfactory heating service. The increased life was due to the shapes being laid on the 2.5″ side and thus only this series of narrow edges were presented at the top of the checkerwork for the collection of flue dust.

General Considerations

The service conditions obviously must be of first importance in the selection of refractories for various uses in a furnace, and many of them are definitely known but it must be remembered that it is rather difficult to determine the exact conditions of gas composition, temperature and fluxing by fume and small slag particles, and not much exact information of this kind is available at present.

Of the different grades of steel, high carbon steel is least severe to the open hearth since the slag is neither as oxidizing nor is the time as long as in a low carbon steel process. Since the melting temperature decreases and fluidity of a steel increases with the carbon content the production of low carbon steel requires either a furnace temperature several hundred degrees higher than the high carbon steel process, or a much longer treatment, and greater wear and tear of the furnace results. If a charge of 75% scrap and 25% pig be "melted down soft," thus producing an extremely corrosive slag and a heavy oxidation of the scrap, the slag corrosion resulting is quite severe especially in the acid hearth furnace. If an extremely active slag is not used, the time of the operation must be increased in order to remove the carbon, and the furnace wear and tear is correspondingly increased per heat.

If a large quantity of pig iron is used, its quick oxidation by the ore added causes much more splashing of slag on the lining than when lower amounts of pig iron are used.

The practice of carrying at all times 0.15 Si and 0.20–0.40 manganese as residual silicon and manganese in the bath in order to keep oxygen out of the final steel, removes the oxidizing layer of the bath between the metal proper and the slag, and thus materially decreases the corrosive action at the shallow edges of the bath.

In the final analysis, the refractory which is most desirable from the steel maker's point of view is that which will enable him to produce steel at the lowest furnace cost per ton. If by frequent renewals of lining at a fairly low price, a fast working furnace will produce a production large enough to offset the cost of new linings, that operation is satisfactory.

If a higher priced refractory will permit the furnace production to be sufficiently increased to result in a lower or equal furnace cost per ton of steel, that refractory is desirable.

In conclusion the author wishes to acknowledge and express his appreciation of the aid in obtaining information given him by W. H. Kelley, Refractories Engineer of the Bethlehem Steel Company, and by Bradley Stoughton, Professor of Metallurgy at Lehigh University.

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CALCINING AS AN AID TO GRINDING[1]

By W. M. Myers[2]

ABSTRACT

Experiments show no value commensurate with calcining and of water quenching of quartz.

Fire was commonly used in the early days of the mining industry to soften rock, so that it could be excavated more readily with the crude tools available, and to facilitate the crushing of ores in primitive metallurgical processes. Although gunpowder was first used for blasting in 1627, it was not generally adopted as a mining explosive until a much later date, and the ancient process of "fire-setting" was persisted in until the nineteenth century in some European mines.[3]

Twenty years ago it was customary to calcine some feldspars before grinding, particularly the soda feldspars in the eastern Pennsylvania district. Calcination of feldspar has been largely abandoned, and it is probable that the most conspicuous example of the survival of calcining is in the preparation of flint and quartz for the ceramic industries.

The bulk of the material calcined at present is imported French flint pebbles; a lesser amount of massive quartz is also calcined before grinding. This quartz is used as a filler and as an abrasive, as well as in ceramic wares. The flint is commonly calcined in small bottle-shaped kilns which have a capacity of 15 tons. These kilns are charged with alternate layers of flint and wood, one cord of wood being necessary for 15 tons of flint; the charge is ignited and is allowed to burn for 36 hours, after which the kiln is drawn. The calcined flint is crushed under chaser mills to $^3/_8$ inch and then ground for 6 hours in silex lined tube mills with flint pebbles. Before calcination the flint is a dense, even-textured, tough, gray stone. After calcination it becomes an opaque white in color, and is partially shattered through the development of fractures which apparently should greatly facilitate grinding.

The quartz which is calcined is coarsely crystalline and consists of nearly 100% silica. The flint is cryptocrystalline and generally contains about 98% silica. A typical flint analysis is as follows:[4]

Silica	98.16%	Magnesia	0.20%
Alumina	.25	Soda	.20
Iron oxide	.05	Potash	.24
Lime	.50	Loss on ignition	.52
			100.12%

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[1] Published by permission of the Director, Bureau of Mines, Department of the Interior.

[2] Associate Mineral Technologist, Non-metallic Minerals Station, Bureau of Mines (in coöperation with Rutgers University, New Brunswick, N. J.).

[3] Hoover, "De Re Metallica, Agricola," p. 118.

[4] Analysis from Golding Sons Co., Trenton, N. J.

Calcination causes no change in chemical composition other than removal of the material lost on ignition and complete oxidation of the small amount of iron present.

It was stated by one of the largest producers of calcined flint that the cost of the operation for both fuel and labor averages one dollar a ton. In order to determine if this calcining cost is warranted a considerable number of comparative grinding tests were made.

The calcined flint used in these tests was obtained from a commercial kiln where it had been subjected to the usual 36-hour burn. Uncalcined flint pebbles having the same dimensions were selected from the same source. These materials were crushed in a jaw crusher and then ground in a small pebble mill with flint pebbles and the various products sized at intervals to determine the grinding efficiency. Care was taken to have all conditions affecting the grinding of the two materials identical. The pebbles were fed directly to the jaw crusher which was set to have a gap of $^1/_4$ inch. A sized feed, 14 to 28-mesh, was prepared for the pebble mill so that the materials would be identical in size at the beginning of the pebble mill grinding. This size was found to be best suited to the capacity of the mills.

In commercial work flint is rarely quenched but is permitted to cool in the air. Quartz, however, is frequently quenched with cold water. To determine the effect of quenching, a batch of flint pebbles was calcined in a muffle furnace and divided into two portions, one of which was quenched while hot by immersion in cold water; the other was permitted to cool slowly in the air. The quenching shattered the flint considerably and the quenched product broke more readily in the jaw crusher so that a smaller amount of the coarsest material was produced than was formed from the unquenched flint. In the smaller sizes little difference was noted, and further grinding in the pebble mill showed little difference in their grinding properties.

These figures show that the grinding efficiency of flint is considerably increased by calcination apparently because of the inversion of the quartz from α to β form at 575°C and the accompanying volume change of over 2%.[1] This volume change produces minute fracturing and furnishes planes of weakness along which the flint separates. Quenching aids only by producing the coarsest fractures. The increase in grinding efficiency is most marked in the material ground in the pebble mill for six hours. After this grinding 92.8% of the calcined flint passed a 325-mesh screen while only 70.1% of the uncalcined material could pass this screen.

The results are tabulated in Table I.

Definite information is lacking concerning what temperature is attained

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[1] W. L. Shearer, "Effect of Flints on the Thermal Expansion of Some Whiteware Bodies," *The Ceramist,* [6], 143–65 (1924).

TABLE I

Mesh	Jaw crushers, 1/4-inch gap				Pebble mill, original feed, 14 to 28-mesh					
					At end of 1 hr.		At end of 3 hr.		At end of 6 hr.	
	Laboratory calcined flint, %	Laboratory quenched flint, %	Uncalcined flint, %	Commercial calcined flint, %	Uncalcined flint	Calcined flint[1]	Uncalcined flint	Calcined flint[1]	Uncalcined flint	Calcined flint[1]
+ 4	70.6	64.2	75.8	67.9						
− 4 + 8	15.9	20.2	12.5	16.4						
− 8 + 10	4.5	5.6	3.8	5.0						
− 10 + 14	2.8	3.2	2.4	3.0						
− 14 + 28	3.1	3.6	2.8	3.7	30.4	25.4	0.3	0.1	0.0	0.0
− 28 + 35	1.0	1.1	0.8	1.3	25.2	26.9	1.2	0.1	0.0	0.0
− 35 + 48	0.6	0.7	0.5	0.8	13.4	14.4	6.8	0.9	0.0	0.0
− 48	1.5	1.4	1.4	1.9						
	(100.0)	(100.0)	(100.0)	(100.0)						
− 48 + 65					9.2	9.9	22.3	11.8	0.0	0.0
− 65 + 100					5.8	6.4	16.4	25.1	0.1	0.0
−100					16.0	17.0	53.0	62.0		
					(100.0)	(100.0)	(100.0)	(100.0)		
−100 + 150									2.5	0.1
−150 + 200									9.7	1.1
−200 + 250									5.8	1.0
−250 + 325									11.8	5.0
−325									70.1	92.8
									(100.0)	(100.0)

[1] Material for these tests was commercially calcined.

in the kilns. It probably varies greatly but can hardly be expected to exceed 800° or 900°C. Attainment of higher temperatures would increase the expense of calcination and might have an undesirable tendency to produce cristobalite.

The balance of the increased efficiency in grinding against the cost of calcining appears to be a close one. The crushing of uncalcined flint is complicated by the toughness and the shape of the pebbles and also by the necessity of avoiding any contamination by metallic iron. A jaw crusher with manganese steel jaws should crush the flint satisfactorily to a suitable size for pebble mill feed and could be substituted for the chaser mill. This has already been done in modern feldspar mills. The increased efficiency of grinding calcined flint in the pebble mill does not appear to be sufficiently great to warrant a calcining cost of a dollar a ton. The difference, however, is too small to justify any extensive alterations in plants now in operation. The difficulty of crushing uncalcined flint pebbles with a chaser mill may be the chief reason for adhering to the calcination method. A decrease in the use of chaser mills and the employment of more modern crushing equipment may be expected in the future, and it is probable that this use will be accompanied by a decline in the practice of calcination.

SHALES OF NORTH CAROLINA[1]

By Jasper L. Stuckey

ABSTRACT

North Carolina contains several extensive areas of shale deposits, which are favorably located for working and which in their slightly weathered condition have been recently found to be well adapted to the manufacture of face brick, hollow blocks, sewer pipes, etc.

As a result of these discoveries a number of clay working plants have been recently set in operation and others are in course of construction.

For a number of years North Carolina has been one of the leading states in the production of high-grade residual kaolin such as is used in the manufacture of china, porcelain and spark plugs, but it is not ordinarily thought of as containing deposits of shale suitable for the manufacture of face-brick and high-grade heavy clay products, and in the literature very few references to North Carolina shales are to be found. Ries[2] pointed out, in the second edition of his textbook on clays, that a weathered shale was being used at Pomona, Guilford County, for the manufacture of sewer pipe and further stated that Triassic shales were known to occur in the state, but that little was known of their value for making clay products.

In the reports of the State Geological Survey considerable space has been devoted to clays and clay products, since 1897, but the first reference to shale was published in 1914.[3] This report pointed out that this material was then used in Guilford County and that plans were being made to develop a shale deposit in Madison County a short distance west of Asheville.

Due possibly to the abundance of timber in the state and also to the fact that the methods in use at the various brick plants of the State were suited to the use of clay and not readily adapted to the use of shale, little or no progress was made in its application until after 1920. About this time both the brick makers and the users of clay products realized that all the face-brick and high-grade heavy clay products used in the state were being imported and that with building going on at such a rapid rate the State would be a heavy loser in the added cost of clay products used in building unless these materials could be manufactured at home. This loss was even more evident to the brick makers who were feeling the demand for a high-grade product. Consequently during the years 1921 to 1924 investigations of the shale resources of the State were made by the more

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[1] Recd. Aug. 14, 1925.

[2] H. Ries, "Clays, Occurrence, Properties and Uses," 2nd ed., N. Y., 1908 (John Wiley and Sons).

[3] "The Mining Industry in North Carolina during 1911 and 1912," N. C. Geol. Survey, *Economic Paper*, **34** (1914).

progressive manufacturers, encouraged and assisted to some extent by the State Geological and Economic Survey. This work has been materially increased during 1924–25 by the help of the Department of Ceramic Engineering of State College, Raleigh, N. C., under the direction of A. F. Greaves-Walker.

The results of these investigations have shown that there are in the State deposits of shale, which, although small when compared with those of such states as Pennsylvania, New York and Ohio, are more than adequate to meet the needs of the State once they are properly utilized.

When referring to shale it is to be understood that the material used is in at least a slightly weathered condition, which tends to increase its plasticity. The absolutely fresh rock, especially that of the slate belt, is of doubtful value. The change due to weathering apparently extends to a depth of 30 to 50 feet.

The map (Fig. 1) shows the general distribution of those geological formations in the State which contain shales that are now considered of commercial value. These shales, which belong to three different geological formations, are found in four areas conveniently located to all parts of the State. These known areas are: (1) The pre-Cambrian slate belt of the central part of the State, particularly that portion of it in Davidson, Stanly, Anson and Union Counties; (2) The Cambrian shales near Hot Springs, Madison County; (3) The Triassic shales of the Dan River Coal Field in Stokes and Rockingham Counties; and (4) The Triassic shales of the Deep River Coal Field in Durham, Chatham, Lee, Moore and Anson Counties.

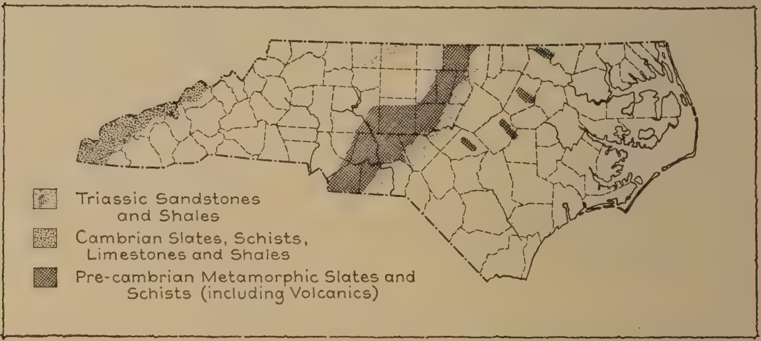
Triassic Sandstones and Shales
Cambrian Slates, Schists, Limestones and Shales
Pre-cambrian Metamorphic Slates and Schists (including Volcanics)

FIG. 1.—Map showing distribution of shale in North Carolina.

Pre-Cambrian Shales of the Slate Belt

The largest area of shales in the State and the one that has been best investigated and developed for the face-brick industry is that of pre-

Cambrian slates, commonly known as the "Slate Belt," which crosses the central part of the State in a northeast to southwest direction. This area has long been of scientific interest and was early recognized by geologists as of pre-Cambrian age, but it was only recently that its value as a source of shale for high-grade products was discovered. The formations of the area consist of a great volcanic-sedimentary series made up of long bands of shale, composed in part of volcanic ash and in part of land waste. The whole series has been so completely metamorphosed over most of the area that the shales have become slates with a well defined cleavage, which has in most cases destroyed the bedding planes. In parts of Stanly, Anson and Union Counties metamorphism was less severe and as a result cleavage planes are not so well developed while the bedding planes have been very little disturbed leaving large areas of shale little altered and almost horizontal. This part of the area is most important as a source of shale. Weathering has attacked the shales to great depth so that in most places they are fairly soft and readily worked.

These shales first began to attract attention in 1921 when two or three companies, particularly those at Norwood and Monroe, which had been using surface clays and making common brick, investigated the underlying shales, found them of value and began converting their plants into modern face brick plants.

In January, 1922, the Winston-Salem Southbound Railroad had shales collected from seven possible plant sites along its line in Stanly and Anson Counties and tested by Ellis Lovejoy[1] at Columbus, Ohio. The report of these tests shows that six of these shales have a firing range of 7 to 9 cones (1958° to 2246°F) for a good red color and hard product. All the shales are reported as working well in machine tests, but require a maximum amount of pugging to get the best results. In the wet state they are weak, and cannot be classed as strong in the dried state as compared with other clays and shales, but they have ample strength to withstand all the weight in the kilns to which the bottom brick are subjected. The drying behavior of all the shales tested is excellent. The drying shrinkage of the different samples varied from 1% to 5%. The firing shrinkage is greater and inclined to be high. In one sample it varied from 1.1% at the lower temperature to 8% at the higher temperature and was classed as almost ideal. In the other samples it varied from about 1% at the lower temperatures to 11.5% to 13.3% at the maximum temperatures. The six shales tested have a long safe firing range for a steel hard product and good red color. A vitrified product is possible but not encouraging for a paving brick. The conclusion of the report is that these shales are ideal for brick, hollow blocks up to 5 x 8 x 12 inches, and drain tile up to a diameter of nine inches.

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[1] Ellis Lovejoy, Lab. Test No. 3110. Report of the result of test of shales between Whitney and Ansonville, North Carolina along the Southbound Railway, for the Winston-Salem Southbound Railway Company, Winston-Salem, N. C. Used by permission of the President of the Winston-Salem Southbound Railway.

Actual usage at the different plants shows that the shale can be readily made into good common brick and face brick if properly handled. No attempt is at present being made to manufacture any other product. The shale is weak in the wet state but not to such an extent as to require detailed preparation. A dry pan for grinding, and thorough pugging have been found entirely satisfactory. The shrinkage is often high but this can, with proper handling, be overcome. No trouble is found in firing the weathered material, but the harder (less weathered) layers, however, are more difficult to handle due to the fluxes present, and because of their frequently short firing range which is often not over 50°F. This less weathered material will often not stand over 1850°F.

The shale fires a deep red color and makes ideal face brick of the variegated color so much in demand now. Beautiful colors are produced naturally, and by flashing and the use of chemicals the range can be easily and considerably increased. These shales will doubtless make good drain tile of the smaller sizes, building tile, and floor and roofing tile if the shrinkage is properly cared for.

Four modern shale brick plants, with round down draft kilns, located in Davidson, Stanly and Union Counties in the southern part of this area will produce in the year 1925 at the present rate of manufacture a minimum of 40,000,000 face brick.

These developments are just beginning to indicate the value of the shales in this district. The supply in the southern half of the area is large and any number of suitable plant sites can be found convenient to railroad transportation. Little is as yet known about the northern half of the belt where the shales are more highly metamorphosed.

Deposits of this same type of shale that are interesting and may prove of value are also known in Harnett, Johnson, Nash, Halifax and Northampton Counties.

Cambrian Shales

Formations of Cambrian age are found in a number of localities in the western part of the state, the most important shale deposits of this age being found in Madison County near Hot Springs. These shales are conveniently located near the main line of the Southern Railway from Asheville to Knoxville, Tenn., and have been known for several years. An attempt to work them in 1917–19 proved a failure due to the lack of proper equipment. The shales are red firing and appear to have good working qualities and will doubtless prove of considerable value for heavy clay products when they are properly worked.

Triassic Shales—Dan River Coal Field

A belt of Triassic rocks about five or six miles in width, commonly known as the Dan River Coal Field crosses Stokes and Rockingham Counties in a northeast-southwest direction. The formations consist of interbedded sandstones and shales which dip from 30–65° to the northwest. Important shale deposits varying from a few feet to 300 feet in thickness are abundant throughout the area. Due to the attitude of the beds it is comparatively easy to open a shale pit on any one of them and work along the strike.

This was the first shale area in the state to be successfully worked. For a number of years the Pomona Terra Cotta Company at Pomona, Guilford County, has been getting its supply of shale from beds in this area near Madison, Rockingham County. Pits have been worked to a width of 60 feet, a depth of 40 feet and from a few hundred to 2000 feet along the strike.

The shale is dug by steam shovels, loaded into gondola cars and shipped 30 miles to Pomona where this Company has the largest and best equipped sewer pipe plant in the South. The works now consist of four modern sewer pipe plants, with 44 round kilns, having a capacity of approximately 5000 tons of sewer pipe per month. A high grade vitrified product that will pass all A.S.T.M. specifications on absorption and crushing strength, is being produced.[1]

In the same area at Pine Hall, Stokes County, the Pine Hall Brick Company is producing a high grade face brick. This Company has a thoroughly modern shale brick plant with a capacity of about 20,000,000 bricks a year.

These shales are naturally soft and work exceedingly easy. They have a low shrinkage, are red firing, and produce a dense body of pleasing color at temperatures around 1850–1900°F. They are well suited for face brick, with a wide range of natural colors, as well as sewer pipe, drain tile, hollow building tile and other clay products. The quantity of shale available in this area is large and well supplied with transportation facilities.

Triassic Shales—Deep River Coal Field

The most promising and least developed shale area in North Carolina is the Deep River Coal Field of Moore, Chatham and Lee Counties with its extension to the north and south.

This area is some 12 miles wide and 75 to 100 miles long with Sanford, Lee County, as its center.

The formations consist of interbedded sandstones and shales of Triassic age, which vary in thickness up to several hundred feet and dip from

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[1] A. F. Greaves-Walker, N. C. State College of Agriculture and Engineering, *N. C. Agric. and Indus.*, **2** [11] (1924).

20–60° to the southeast. The dip of any given bed makes mining in most cases extremely easy.

Considerable interest is being shown in the shales of this area. Two plants near Sanford are making excellent brick while two plants for the manufacture of hollow building tile are in the process of erection. The Carolina Fireproofing Company, Charlotte, N. C., is completing a plant near Gulf. The kilns will be fired by producer gas made from coal obtained at the near-by mines on Deep River. The Borden Brick and Tile Company, Goldsboro, N. C., is building a modern tile plant near Sanford, Lee County.

The shales of this area are red firing and develop an attractive color in the kiln. They are naturally soft and have unusually good working qualities and low shrinkage. At the low temperature of around 1800°F they fire to a dense body with a clear ring. At the plant of L. C. Isenhour near Colon, Lee County, the typical shale has a shrinkage of 1 to 4% and fires to an excellent red color and dense body with a clear ringing sound at 1750–1800°F. These shales are well suited for the manufacture of common and face brick, hollow building tile, drain tile and sewer pipe. The area contains an abundance of shale with a large number of plant sites readily accessible to railroad transportation.

North Carolina has in the past obtained large quantities of face brick and high-grade heavy clay products from other states. In the near future however, with proper utilization of the shales of the state as they are now known, producers should be furnishing practically all the clay products needed at home and also shipping to the neighboring states.

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INTRODUCTORY STUDY OF THE PUGET SOUND SHALE AND GLACIAL CLAYS[1,2]

BY THAD. O. SMITH

ABSTRACT

Type and character of clays of Puget Sound are described.

Geologists tell us that a million or more years ago an older mountain range stood in the present location of the Cascade mountains. On the western side the lower elevations were covered with swamps, lakes and shallow arms of the ocean. Rank growing vegetation and a tropical climate existed. In the course of time, as the mountains were weathered and eroded, clay was formed, carried down by the streams and deposited in the shallow waters along with the rotting vegetation or carbonaceous material. These sediments increased in thickness, were subjected to pressure resulting from their own weight and later crustal movements and have been tilted, faulted and broken until we have the present shale, sandstone and coal beds of Pierce and King counties.

A certain amount of intermingling occurs between the three types of sediments. The carbon, sand and clay content of each is subject to wide variation. Because of the carbonaceous matter in the shales, a large part of the iron is usually in the ferrous or reduced condition and tends to give the burned shale products a brown instead of the deep red shades. The clays and shales which have been lying out in the open and have become thoroughly oxidized, such as those found in eastern and southwestern Washington, give better red colors than those which are mined from underground. These shales are exposed in a number of places such as Renton, along the Cedar and Green rivers and at Bellingham. Wherever coal is found, shales can be expected to occur, though they may not always be of sufficient purity to be useful.

The plasticity of the shales as mined is almost a negative quantity. This is due to the tightly packed structure which has been produced by the pressure and some chemical action. If the pressure were continued long enough the shale would become slate. The original plasticity is best restored by grinding with water in a wet pan, as in sewer pipe manufacture, although for most wares, sufficient plasticity is developed by the dry-pan pug mill process.

An analysis of a local shale showed 6% volatile matter, which is a mixture of chemical water and carbon, and about 0.2% sulphur. The latter gives oxidation troubles in the kiln and also is one of the causes of scumming and efflorescence found on the surfaces of the fired ware.

The shales are used in a number of different products but find their best

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[1] Recd. Apr. 9, 1925.

[2] Presented at the Pacific Northwest Clayworkers' Association, Jan. 17, 1925.

application in the manufacture of sewer pipe, paving brick, face brick, tile and other structural products. A comparison of the local commercial shales with some eastern United States shales shows that those of the Puget Sound district are vitrified at lower temperatures but have a shorter firing range. This is best shown by a comparison in the following porosity table.

TABLE I

APPARENT POROSITY[1]

Cone	Average Puget Sound shale	Average Puget Sound glacial clay	Purdy's Classification[2] Paving brick	Sewer brick	Bldg. brick
08	33%	33%	29 + %	24–29%	18–24%
06	31	30	26–35	14–26	5–14
04	25	18	19–33	7–19	4–7
02	17	4	18–32	2–18	...
1	9	1	17–31	2–17	...
3	6	Fused	7–13	2–7	...
5	3	Fused	3–6	2–3	...
7	5	Fused	2–4	2–2	...
9	Fused	Fused	1–2	...	...
11	Fused	Fused	1–2	...	...

Puget Sound Glacial Clays

The glacial clays which are very plentiful in the Puget Sound region are of comparatively recent origin, being deposited from 30,000 to 40,000 years ago. After the deposition of the shales, the second or our present Cascade range was gradually elevated into its present position and the climate changed from tropical to arctic. Glaciers crept down from the north and were joined by smaller feeders from the Cascade and Olympic ranges. Two, possibly three, distinct flows occurred, each following three main channels: that of the Sound itself, the Hood Canal route and the third pushed its way from Everett to Snoqualmie. The natural drainage channels were all blocked and numerous lakes were formed from the melted ice. In the quiet waters of these lakes the fine rock flour and suspended clay materials were deposited and have formed accumulations of considerable depth. Many of these lakes have remained until present times and the clay washing process is still continuing at a much slower rate. The second glacial period followed the first after some interval of time, but the ice traveled the same channels to points farther south. The terminal moraines in the neighborhood of Tenino and Olmypia show the extent of the ice sheet. These vast accumulations of sand gravel and clay were carried in part down the Chehalis river valley but the remainder served to block the water from the melting ice. The larger lakes were drained through the straits of Juan de Fuca after the retreat of the glacier to the north. The sediments exposed have received comparatively little pressure and show no fissile structure as do the shales, but may vary considerably in sand and gravel content. Practically no crustal movements have tilted the beds or changed them from their original positions.

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[1] Per cent apparent porosity equals the percentage weight of water absorbed by the fired body in terms of the bulk volume of the piece. The percentage absorption is approximately one-half of the per cent apparent porosity.

[2] Purdy's classification, "Paving Brick and Paving Brick Clays of Illinois," Ill. Geol. Surv., *Bull.* 9, 275 (1908).

Our blue-gray glacial clay represents the mixing of sediments and rock flour from wide areas of land which the ice has ground to powder by its weight and movement. As the ice passes over a clay or shale formation it will pick up the surface and mix the plastic materials with the non-plastic rock dust. The glacial clays sorted out from such a heterogeneous mixture contain a large amount of very fine sand and hence are not as plastic as one would first think. A sample from a local brick plant gave only 5% sand that would not pass a 200-mesh screen. However, as this is our finest screen, the total amount of non-plastic material was determined by settling the clay in water and siphoning off the plastic or floating material. The settled material was rewashed until clear water could be decanted after one minute settling. The total amount of sand was found to be 40%. However, this is a very necessary ingredient to hold the shrinkage down to normal.

The sand content varies widely in amount in different localities and is made up of a mixture of different minerals. Quartz, lime and soda feldspar and zircon have been identified under the microscope. An analysis of a glacial clay showed 2% volatile matter which consists of both combined water and carbonaceous matter; 0.014% sulphur was present as sulphate while the total content of sulphur was 0.082%. The sulphates are the cause of most of the scumming found on the soft fired brick. The volatile matter found in the glacial clays is much lower than that found in the shales because of the lower carbon content.

Many of the eastern and middle western glacial clays such as those found through Illinois, Indiana and Ohio contain quantities of both finely divided and coarse limestone picked up by the ice as it traveled south from Canada. Limestone if it is not finely powdered causes spalling and popping due to the slaking and swelling of the fired lime in the brick when moisture and carbon dioxide combine with the quicklime. Our local clays give no trouble from this cause unless an occasional clam shell bed is unearthed in the clay pit.

Glacial clay is used extensively for making face and common brick, building and drain tile. The Portland cement companies mix it with ground limestone to make cement clinker and the concrete men use the Portland cement with glacial sand and gravel to produce concrete; hence, all told, the Portland cement industry in this district is greatly dependent on glacial materials.

For brick manufacture the glacial clays have several advantages and disadvantages: The clays lie on the surface, are easily accessible and are found close to the large centers of consumption. However, in most cases they vary considerably in sand and gravel, usually require some stripping and some method for removing pebbles. They should be mixed in large quantities to preserve a constant uniformity. Much difficulty is experienced by sliding in wet weather, and large quantities of very sandy clay may cover the face of the more plastic material. The glacial clays are soft, grind easily and quickly produce their maximum plasticity. The longer a shale is ground the more plastic and sticky it becomes, and the more water necessary for plasticity. The glacial clays do not have the toughness of the shales, but with their larger quantities of fine sand show more brittleness in the column from the auger machines. Carefully balanced dies are often necessary and thin members are avoided. The vitrification range is very short so that the difference in temperature usually experienced in the large kilns will produce both overfired and underfired brick. The shrinkage on one end of a brick is often much different from that of the other end. Because of the low temperature necessary and the ease of overfiring the glacial clays, wood has been found to be a good substitute for coal. Wood has a long comparatively cool flame which gives better oxidizing conditions and thus produces better red colors than the hotter and more violent coal flame.

Few localities in the United States can furnish clay suitable as slip clays for glazing stoneware, electric insulators, etc. The most prominent are found near Albany, New York, in Texas and Michigan. The Albany slip clays are perhaps the best known and have been formed by glacial action in a very similar fashion to those clays of the Puget Sound district. They have the same blue-gray color when fresh which turns to a dirty brown after exposure to the atmosphere as the iron oxidizes.

Several good mahogany brown slip glazes have been made in the ceramic laboratory with the fine grained local glacial clays mixed with fluxes like feldspar and fired to cones 6–8. Slip clays must not blister or bloat when fused or shrink excessively during the drying period or the early stages of firing.

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THE APPLICATION OF PEBBLE OR BALL MILLS IN ENAMELING[1]

By Edw. W. Lawler

ABSTRACT

A description of pebble mills in enameling is given; details of design and results are discussed.

The size of a ball or pebble mill depends on the amount of material to be ground. For one cubic foot of the dry frit, the mill should be four cubic feet inside the lining and two cubic feet of pebbles should be used. The water added should be in about the proportion of 35 to 40% of the frit volume.

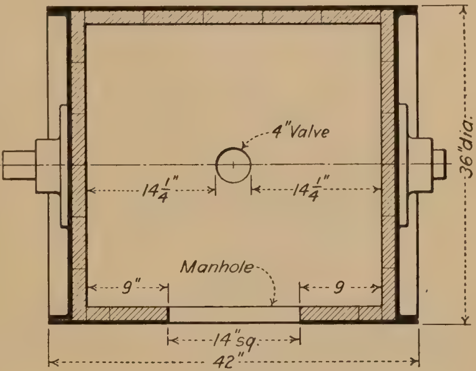

Fig. 1.

The diameter of the mill should not be less than the length. Figure 1 shows a mill 36 inches diameter by 42 inches long. The manhole is in the center and is approximately 15 inches square, so that the distance from the inside of the head lining to the edge of the manhole is about 9 inches. If a 4-inch valve is used as in wet grinding, it will be $14^1/_4$ inches from the ends. In this size mill this is not so bad, but in a mill 8 feet long as in Fig. 2 it is a bad condition as the distance from the head of the mill to the edge of the manhole is 35 inches.

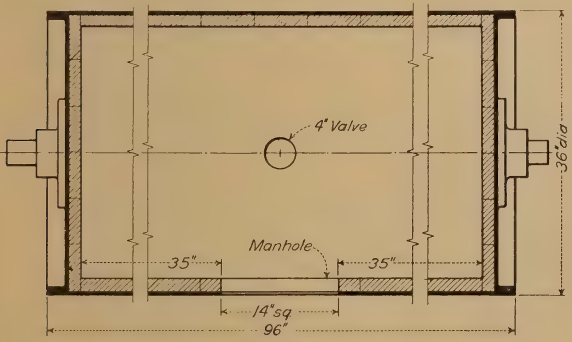

Fig. 2.

In discharging a wet batch, the wet material in the center of a large mill runs out first, while that on each side of the outlet gradually drains out, except that which has settled and separated from the water. This adheres to the pebbles and the lining. If not washed out it will stay in the mill and become part of the next charge. This is the reason the length of the mill should not exceed the diameter.

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[1] Presented at the Annual Meeting, American Ceramic Society, Columbus, Ohio, Feb., 1925. (Enamel Division.)

Cylindrical vs. Sloping Sides

A mill with sloping sides overcomes these discharging difficulties. In a mill which has the same cubic capacity but has sloping sides, the diameter can be 42 inches and the length 14 inches. The manhole would extend the entire width of the cylinder. The 4-inch discharge valve would be only 5 inches from the head. Because of the large diameter and short barrel length this mill would grind the same charge in less time than would the cylindrical mill. It would not be necessary to turn it over when discharging a wet batch and in dry grinding practically all of the charge would run out if the mill were left with the grate down. A minimum of revolving would be required and there would be less breaking of pebbles and lining.

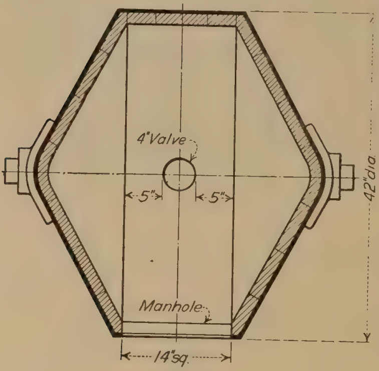
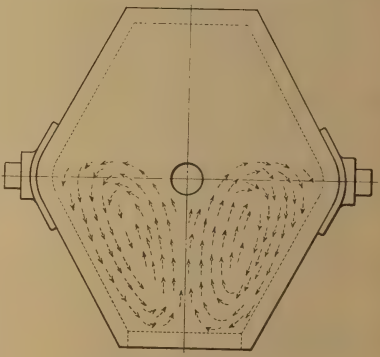


FIG. 3.

The old Alsing mills were 30 inches in diameter by 18 inches long with a manhole the entire width of the mill, a proportion which cannot be improved upon except to increase the diameter.

One of the disadvantages of a cylindrical mill is the flat heads. In a cylindrical mill the head lining is rubbed and worn with a minimum of grinding because the particles of frit do not remain long enough between the round pebbles and the mill head. The sloping sides permit more action of the pebbles per lift of pebbles.

The sloping sided mill must have a larger diameter than the cylindrical mill of equal cubic capacity. The cylindrical mill 36 inches diameter by 42 inches is the equivalent of a sloping sided mill 42 inches diameter but only 14 inches wide. The sloping sides are not patented. The advantages of this type mill are obvious and have been proved by two years' operation.



Path of Pebbles in Mill of Sloped Sides

FIG. 4.

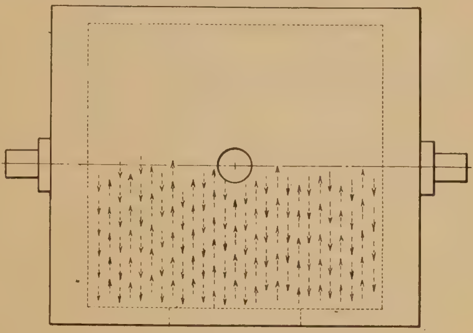
Details of Design

The Manhole The iron on the manhole frame and the cover of a popular size mill now in use present to the action of the pebbles about 50 square inches of iron. White enamel free from black spots cannot be ground in this mill. I have seen covers taken off a mill grinding white frit when brown iron water would run down into the charge from the iron manhole. (See Fig. 5.)

The manhole frame of a mill should be flush with the shell of the mill and not with the lining. (See Fig. 6.) Instead of a $^1/_2$-inch cast iron flange, 16-gage brass, steel or other material may be used.

The Lining A mill with the lining half worn grinds better than a new lining because the square corner is now rounded so that the pebbles fit. (See Fig. 7.) A sloping side mill has no corners.

In lining a mill the best porcelain is none too good. I have just relined a number of mills and the old linings were worn in spots right down to the shell while the adjoining brick were almost as thick as the new ones. This is because the brick were of varying hardness. Soft ones wear out first and new linings are required. Not only does a poor brick wear quickly, but it enters the charge being ground. A hard white porcelain will last longer.



Path of Pebbles in Cylinder Mill

FIG. 4*a*.

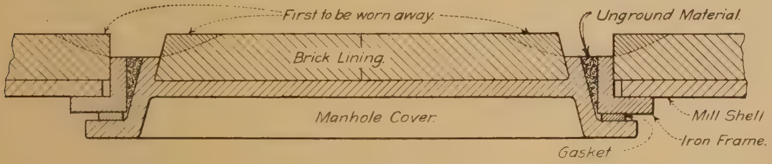


FIG. 5.

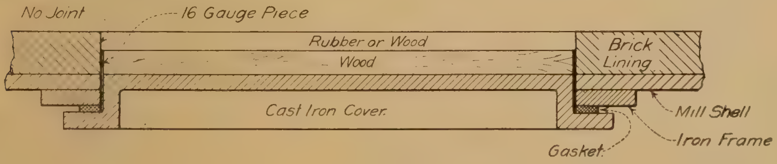


FIG. 6.

A brick with a tongue and groove will not hold in place better, neither will it allow smoother lining. When the lining wears down to the tongue and groove the brick will chip and wear rapidly. A tongue and grooved lining is not easily patched. (See Fig. 8.) The standard keystone shaped brick is the best and if properly set will not fall out because the cement and shape hold the brick.

A first-class porcelain brick costs at the pottery about 7$^1/_2$ cents per pound. A cheaper brick costs 5$^1/_2$ cents.

Silex makes a good lining, but it is rough (an advantage), does not fit closely (a disadvantage), and is very hard to fit by chipping. A silex lining properly set is worth the time for it will outlast any lining except possibly rubber.

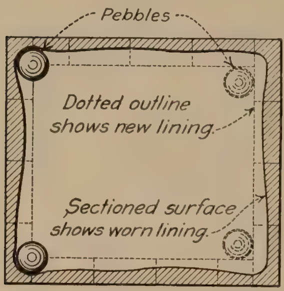
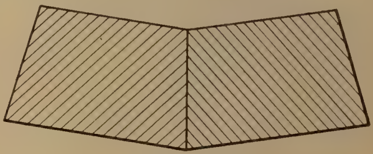

Pebbles
Dotted outline shows new lining
Sectioned surface shows worn lining

FIG. 7.

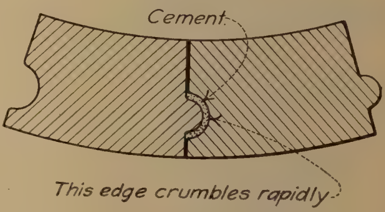
Rubber will outwear the hardest steel. I have seen the inside of a tube mill loaded with steel balls after grinding silver for 90 days continuously. Apparently the lining was not worn, though at the beginning it was only $^5/_8$ inch thick. It is patented and put on the market by B. F. Goodrich Co. J. Denny and R. B. Watson discovered its use as a ball mill lining.

As a lining for enamelers' mills, rubber will surpass and displace all other materials for wet grinding. Dry grinding develops heat which might deteriorate the rubber. If it can be fastened in and if it does as well in batch pebble mills as in continuous ball mills, rubber will be the lining most used. A rubber plug on a valve in a mill will outwear the porcelain linings although here the wear is the heaviest and it usually projects into the mill. (See Fig. 9.)

The Balls Balls or pebbles used for grinding are one of the factors that affect the work of the mill more than anything else. Porcelain balls of good quality are white and do not discolor the enamel charge. Porcelain balls have been preferred but it appears to me that a porcelain ball has no advantage over flint pebbles. They are made by hand and present more points of contact than a water-worn pebble. But the flint pebble is harder.



Keystone



Tongue and Groove

FIG. 8.

The main thing in a grinding body is to concentrate the greatest weight in each within the minimum of surface area. It is for this reason that metal balls do more work than flint pebbles.

Every pebble has a point of contact with as many other pebbles as it can touch and the grinding is done at these points of contact. The smaller the pebble, the more can be put into a given volume. A mill charge that can be broken down by a 1-inch pebble will, therefore, be ground faster with 1-inch pebbles than with 2- or 3-inch pebbles. Larger pebbles have not as many contact points and cause larger voids.

Loading of a Mill The proper way to load a mill is to fill it half full of pebbles of the smallest size which will do the work. Instead of buying 1-, 2-, 3- and 4-inch pebbles and wearing them down to the right size you had better lease this job to the ocean. It costs less.

New pebbles often are dumped from the bags directly through the manhole without regard to the iron, sulphur or other dirt which the enamelist would not care to see dumped into his enamel.

Considering that bags are used more than once and have been containers for various materials, and that they are porous and have many materials dumped on and in them, care should be used not to have these deleterious foreign materials dumped in a mill with pebbles.

A pebble to do its best work in a grinding mill must take the longest roll from the top of the load and must do this with maximum rapidity. When it reaches the top as the mill is revolving, it is a fight between gravity and centrifugal force. If the mill speed is too high it will cause the pebble to carry too high and drop. If it is not quite high enough the pebble will leave the crest of the pebble wave and sluggishly roll to the bottom.

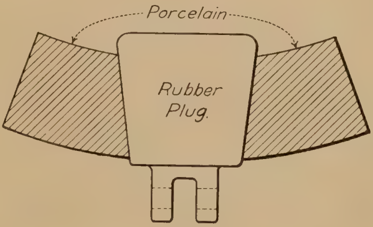


FIG. 9.

The viscosity in wet grinding should be such that the pebble moves freely but not too freely. Too much water causes the pebbles to splash and break. It also washes the material off the pebbles and they grind themselves and the lining instead of the frit. Too little water consumes power up to a point and then decreases the power but increases the time of grinding. It is a simple matter to get the viscosity of the mass right for grinding and add water after grinding if this should be needed for discharging and screening. When the correct amount of water has been determined, a measuring tank holding just that amount should be placed over the mill.

Some claim that the pebbles should roll and not drop vertically but in one plant I know of, they had operated 5 tube mills for ten years at speed sufficient to cause the pebbles to roll. A new manager decided that the drop was better. He speeded up the mills till the pebbles dropped vertically. Now four mills are doing the work which formerly required five mills. In other cases, reducing the speed had no effect on the capacity but lowered the amount of power required. This shows that there is an argument for each method. Checking the operation of the pebble mills may lead to the cause of the troubles and their corrections.

NORTH PLAINFIELD, N. J.

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